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METHODS TO TREAT, CONTROL AND MONITOR SPILLED HAZARDOUS MATERIALS

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A program was instituted to study the feasibility of treating, controlling and monitoring spills of hazardous materials. Emphasis was placed on considering techniques and equipment which would be applicable to general classes of chemicals rather than to specific hazardous polluting substances. Several methods were investigated and found to be promising for removing or detoxifying spills of hazardous chemicals "in situ". These included: the use of sodium sulfide as a precipitating agent for spills of heavy metal ion solutions; the use of activated carbon packaged in porous fiber bags (carbon "tea bags") for adsorbing a wide variety of soluble organic chemicals; and the use of various acids or bases to neutralize spills. Methods were studied to control spills on land and prevent their contaminating nearby surface or ground water. To this end, a four-component "universal gelling agent" was developed to immobilize a spilled liquid. A "cyclic colorimeter", a novel heavy metal ion detector, was perfected and laboratory tested, and a detection kit capable of sensing several chemicals was developed. A computer model was developed and refined to simulate the spread of a spill when certain stream parameters and material characteristics are known. Bioassay studies were conducted for several chemicals using at least three species of biota. In addition, bioassays were conducted to estimate the environmental effect of each of the various treatment methods developed.

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By

Roland J. Pilie, Robert E. Baier, Robert C. Ziegler,
Richard P. Leonard, John G. Michalovic,
Sharron L. Pek, Ditmar H. Bock

Calspan Corporation
Buffalo, New York 14219

Contract No. 68-01-0110
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Project Officer

Joseph P. Lafornara
Industrial Waste Treatment Research Laboratory
Edison, New Jersey 08817

NATIONAL ENVIRONMENTAL RESEARCH CENTER
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

Pollution from spills of hazardous materials is widely recognized as very damaging to the water ecosystem and to the public health and welfare. This report describes several promising new techniques for 1) preventing chemical spills on land from reaching nearby surface or ground waterbodies by gellation in place; 2) detecting and monitoring spills in a watercourse; and 3) treating waters which have been polluted by spills of a wide variety of organic and inorganic hazardous materials.

A. W. Breidenbach, Ph.D.
Director
National Environmental Research
Center, Cincinnati

ABSTRACT

A program was instituted to study the feasibility of treating, controlling and monitoring spills of hazardous materials. Emphasis was placed on considering techniques and equipment which would be applicable to general classes of chemicals rather than to specific hazardous polluting substances.

Several methods were investigated and found to be promising for removing or detoxifying spills of hazardous chemicals "in situ". These included: the use of sodium sulfide as a precipitating agent for spills of heavy metal-ion solutions; the use of activated carbon packaged in porous fiber bags (carbon "tea bags") for adsorbing a wide variety of soluble organic chemicals; and the use of various acids or bases to neutralize spills.

Methods were studied to control spills on land and prevent their contaminating nearby surface or ground water. To this end, a four-component "universal gelling agent" was developed to immobilize a spilled liquid.

A "cyclic colorimeter", a novel heavy metal-ion detector, was perfected and laboratory tested, and a detection kit capable of sensing several chemicals was developed.

A computer model was developed and refined to simulate the spread of a spill when certain stream parameters and material characteristics are known.

Bioassay studies were conducted for several chemicals using at least three species of biota. In addition, bioassays were conducted to estimate the environmental effect of each of the various treatment methods developed.

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SECTION 1

INTRODUCTION

1. OBJECTIVE OF THE PROGRAM. The objective of this program, sponsored under EPA Contract No. 68-01-0110, was to investigate, develop and demonstrate methods to treat, control and monitor spills of hazardous materials. The program was broad-ranging and meeting its objective involved the performance of analytical, laboratory, and field work with hazardous chemicals and consideration of the many conditions of their manufacture, transport, storage, and use.

2. SCOPE OF THE PROGRAM. The program emphasized the development and identification of methods, procedures, equipments, and techniques that will ameliorate the spills of hazardous materials. Second, the scope of the program encompassed all types of chemicals and heavy metal salts; it concentrated on those chemicals and metals that are typical of classes of chemicals and that were deemed most hazardous in a previous study performed by Battelle Institute for the EPA (Ref. 1). (Instrumentation was developed to detect and monitor chemicals in water.) Spills on land as well as in water were of concern; although the feasibility of using some methods to prevent hazardous materials spilled on land from reaching watercourses was shown, methods to treat spills in water were the prime target of investigation. The effects of both the spilled chemicals and the treatment methods on the aquatic environment were studied. Preliminary information was gathered on the costs and logistics of applying treatment methods.

Specific tasks that were undertaken are best summarized in the list below.

(1) Assess existing and develop new methods for treating and controlling spills in watercourses.

(2) Assess existing and develop new methods for treating and controlling land spills.

(3) Develop methods for disseminating and/or applying treatment materials.

(4) Investigate means for reducing toxicity of hazardous materials spilled in watercourses.

(5) Develop detection and monitoring techniques.

(6) Investigate flotation, containment, and skimming operations (as appropriate).

(7) Perform bioassays to determine the effects of countermeasures on aquatic organisms.

(8) Provide limited demonstration of developed techniques where feasible and appropriate.

(9) Evaluate logistics, cost, etc. for countermeasures developed.

(10) Prepare recommendations for programs to demonstrate the effectiveness of the methods developed.

At the direction of the EPA, emphasis within the program in the implementation of these tasks was placed on the test and demonstration of control techniques for near-term operational use and on instrumentation for detecting and monitoring pollutants in watercourses. A second important emphasis was the generalization of the technology developed for application to as many types of chemicals as possible. This was accomplished by classifying chemicals into groups with common physical and chemical characteristics, testing a variety of chemicals from each class in small-scale laboratory experiments to assure common response to a given treatment, and finally demonstrating the applicability of the treatment concept on a selected member of the class in large-scale laboratory or field experiments. A major output of this program is a chart presented in Section 13 that contains recommended procedures for treating and controlling spills of some 250 chemicals.

Important program considerations with respect to methods, treatments, and devices other than the necessity that they be effective were:

(1) The control or treatment method must be capable of being used for a wide variety of chemicals and substances.

(2) The control procedure or techniques must be safe and simple to use.

(3) The equipment and material to be applied must be inexpensive and portable.

(4) The recommended methods for treating the spill should be usable throughout the country.

It is believed that this program has identified, and in many cases tested, many of the best answers currently available for handling spills of hazardous materials. Conclusions and recommendations of the program for improving and demonstrating spill abatement technology are contained in Sections 3 and 4 of this report.

This volume is a summary volume and presents only sufficient material to enable the reader to have an understanding of the work performed, and of the bases for the recommended treatments and demonstrations. Additional material is available to describe in detail the work that was accomplished on:

(1) The treatment of spills of heavy metal compounds.

(2) The experimental work on carbon and resin adsorption.

(3) The design and development of special instrumentation.

(4) The description of immobilization technology for treatment of spills.

(5) A description of the bioassay work accomplished.

(6) The modeling methodology developed in the program.

The reader is referred to this material for substantiative data and a description of the detailed approach used throughout the program.

SECTION 2

SUMMARY

The principal accomplishments of this program may be summarized as follows:

1. ACTIVATED CARBON TREATMENT OF CHEMICALS IN SOLUTION. Extensive experimental and theoretical work was performed on the use of activated carbon for removal of dissolved pollutants from surface waters. Bench scale experiments were performed on twelve organic chemicals ane eight metallic ions, with initial pollutant concentration ranging from 1 to 1000 mg/l and with carbon to pollutant ratio ranging from 1 to 100. Five different types of powdered and granulated carbon and several fibrous carbon products were used. Excellent results were achieved with all organics tested except methanol and with some metallic ions, particularly with Hg^{+2} (99% removal).

The principal problem with the use of activated carbon in natural waters is the removal of the carbon from the water after adsorption is complete. To solve this problem a concept was developed for treating spills with carbon contained in well ventilated, porous bags that are floated in the waterway. These "tea bags" containing the carbon are readily removable from surface waters. Bench scale tests demonstrated that utility of this concept. Tests performed in a simulated stream consisting of a 1 ft^2 cross section, 28 ft long, 8 ft wide race track channel with controllable flow velocity and adjustable bottom roughness were responsible for evolving near optimum bag designs and estimates of time required for treatment under different flow conditions. Tests performed in 12 ft diameter swimming pools demonstrated the importance of a small amount of wave action for providing adequate ventilation in non-flowing waterways. Full scale bags (10 ft long) were used to demonstrate that proper agitation would be achieved with waves as small as 3 inches high. The ease of recovering the carbon-filled bags from either type of waterway was demonstrated. A short operational analysis performed on this concept indicated that a system of nationwide distribution of activated carbon-filled bags for spill removal is feasible and economically achievable.

In addition to work with free-powdered and granulated carbon products and carbon filled "tea bags", bench scale tests were performed on newly developed, experimentally available activated carbon fibers which resemble steel wool. Such products, if ever available at prices comparable to granular carbon, would offer significant advantages in speed of adsorption and therefore pollutant removal efficiency without requiring packaging in porous bags to be removable from a water course.

2. TREATMENT OF WATER SPILLS WITH ION EXCHANGE RESINS. Limited bench scale experiments were performed to examine the potential for using ion exchange resins for removal of dissolved chemicals that do not respond to activated carbon treatment. Significant success was achieved. It appears that the porous bag approach would be useful for dispersal and retrieval of these products. No experiments work was performed with such packaging, however.

3. PRECIPITATION OF HEAVY METALS WITH SODIUM SULFIDE. The treatment of heavy metal compounds by precipitation of insoluble metal sulfides was evaluated. The treatment is applied by introducing sulfide ions, derived from a solution of sodium sulfide, into the spill. A wide range (literally thousdands) of heavy metal compounds can be treated by this method. Bench scale tests were performed on 28 of these compounds on the program. Channel tests were performed to test effectiveness of the treatment in flowing streams and methods for detecting several spilled materials for treatment. Large scale laboratory experiments were performed in 12 ft diameter swimming pools using ferrous sulfate as the spill simulant. Small scale field experiments performed under natural conditions also made use of that harmless stimulant. These experiments demonstrated that small spills can be safely located by injecting small amounts of sodium sulfide into the waterway and noting the location of the visible precipitate and treated by dumping the appropriate quantities of sodium sulfide into the traced spill from plastic bottles.

Large spills require carefully controlled treatment with sodium sulfide to avoid potentially dangerous secondary pollution. An equipment concept was developed in which metallic ion concentration measurements would be used to automatically control the amount of sodium sulfide dispensed and feedback would be used for compensating for measurement errors.

An experimental program was performed to train interested volunteer firemen in the use of these treatment procedures to minimize hazards from small heavy metal spills.

4. IMMOBILIZATION OF HAZARDOUS CHEMICALS. A gelling agent consisting of four active ingredients and one inert powder was developed and tested successfully on 40 liquid chemicals in bench scale experiments. In each case the chemicals were congealed into a thick, viscous mass that would not flow when the beaker was turned on its side. The material was field tested in specially constructed ditches with 1% and 2% grades. In all cases 55 gallon liquid spills were totally immobilized in less than 80 ft by the application of 10 to 25% (by weight) of the agent. Similar tests against liquids floating on water improved the efficiency of crude booms to the extent that 4 inch thick layers of gelled material could be retained with no difficulty. In all cases the gelled material was removed from the surface with shovels and returned to the 55 gallon drums for later disposal.

Narrow slits in tanks were sealed to prevent further spillage by injecting the gelling agent into the slit with sand blasters.

An operational analysis was performed which indicated the feasibility of establishing caches of this material around the nation so that it could be quickly transported to a spill site. The economics of such preparations are reasonable.

Using concentrated sulfuric acid as the spilled material, a large scale experiment was performed to demonstrate that highly reactive materials can be immobilized by absorbing the liquids in fly ash. Neutralizing agents can be placed on the liquid-fly ash slurry for treatment. The reaction rate can then be controlled by controlling the rate at which the neutralizing agent is mixed into the slurry.

Spills of heavy metal compounds absorbed by the ground were immobilized by treatment with sodium sulfide. Movement of the metal sulfide precipitates formed under the surface by the procedure was eliminated except in conjunction with soil in which they were formed.

Using ethylene dischloride as a test material, it was effectively demonstrated that spills of liquids that sink in water can be trapped in excavations in stream beds without interrupting stream flow.

5. DETECTION AND MONITORING. A cyclic colorimeter which uses modulation of indicator injection to reduce sensitivity to natural turbidity and fouling was designed, constructed and tests on this program. A spill detection kit containing conductivity meter, pH indicator, odor samples, and colorimetric reagents was developed and proven effective in tests involving volunteer firemen. Tests were performed of the utility of conductivity meters, pH probes and specific ion electrodes for detection and measurement of spilled acids, bases, and metallic compounds. Catalytic combusters were tested for detection and monitoring of spills of volatile organic solvents.

6. MODELING. Two types of models were developed on this program. In the first type an expression was developed to describe the rate of removal of a pollutant from solution by activated carbon adsorption in terms of three constants that are readily determined by simple laboratory experiments and a parameter which depends on the ventilation of the carbon by the solution in the specific flow (or wave agitation) conditions of the spill.

The second type of modeling effort considered the dispersion of the spilled chemical in a waterway. Two modeling concepts were developed. In the simpler of the two models, the solution to primitive diffusion and flow equations were programmed on a desk top computer to produce plots of the contours of pollutant concentration at any selected time after a spill. The model is intended for use in an on-site, adaptive prediction procedure that makes use of measurements of pollutant concentration made at the spill site to determine the dispersion coefficients to be used in predicting future concentration contours.

The second, a more sophisticated model, includes the possibility of incorporating a treatment effect in estimating the pollutant dispersion. This model permits analysis not only of the concentration distribution of pollutant but also of the mean, variance, skewness, and kurtosis of the distribution.

7. BIOASSAY STUDIES. Toxicity tests were performed with methanol, phenol, acrylonitrile, ammonium hydroxide, acetone, cyanohydrine and chlorine using fathead minnows as test subjects. Additional tests were performed to determine toxicity to the minnows of methods used to treat spilled materials and of reaction products that remain after treatment.

8. HAZARDOUS CHEMICAL/COUNTERMEASURES MATRIX. The final section of this report is a compilation of recommended procedures for treating and controlling some 250 recognized hazardous liquids having a high probability of being involved in spills into or near water courses.

SECTION 3

CONCLUSIONS

Specific conclusions based on work performed on this program are summarized here. Specific recommendations are summarized in Section 4. A generalization of conclusions and recommendations for treatment of spills of 250 of the most hazardous chemicals in the form of a treatment matrix that is useful to the field worker is presented in Section 13 of this report.

1. ACTIVATED CARBON TREATMENT OF CHEMICALS IN SOLUTION. Adsorption on activated carbon is an effective method for removal of many compounds from aqueous solutions.

A dosage of 10 parts of carbon to one part pollutant is a reasonable compromise for spill treatment.

Carbon must be packaged in such a way as to permit removal after adsorption is complete in order to prevent unacceptable esthetic damage and possible toxic bleed off.

Packaging of granular carbon in porous bags, i.e., carbon teabags, is an effective procedure which permits dispersal and essentially complete retrieval without causing a prohibitive decrease in adsorption rate.

A new product, aggregates of carbon fibers that resemble loosely-packed steel wool, which is available in small experimental quantities only, appears to offer similar dispersal and retrieval capability without auxiliary packaging and does not decrease adsorption rate.

The cost of preparations on a national scale for treating spills with activated carbon appears to be reasonable considering the potential benefits.

2. TREATMENT OF WATER SPILLS WITH ION EXCHANGE RESINS. Limited laboratory experiments with ion exchange resins have demonstrated that these products are effective for the removal from solution of some of the chemicals which do not respond to activated carbon treatment. It appears that the teabag technique would be suitable for dispersal and retrieval of these products.

3. PRECIPITATION OF HEAVY METALS WITH SODIUM SULFIDE. The use of sodium sulfide treatment to form heavy metal sulfide precipitates has been shown to be effective in significantly reducing the concentration of many heavy metal ions in solution and thus reducing the immediate hazard of heavy metal spills. But since sodium sulfide is itself toxic, care must be taken in its application to spills.

Since the metal sulfide precipitate formed upon contact with sodium sulfide solutions is usually readily visible, it is appropriate to use the sodium sulfide solution in small quantities to locate the plume of toxic heavy metal compound and define its boundaries in the water body. Appropriate quantities of the treatment may then be added at the proper location to effect the precipitation without creating a secondary hazard from the sodium sulfide. Analysis of existing toxicity data indicates, however, that even if by error the heavy metal spill were completely missed by the treatment, the sodium sulfide would pose a problem that is less than one-tenth as severe as the initial spill. Weighing the potential secondary hazard against the potential reduction in toxicity of the initial spill recommends strongly that the sodium sulfide treatment procedure be implemented for small spills of heavy metal compounds.

The secondary hazard that could result from errors in the treatment of large spills is significant. For this reason, the treatment of large spills should be based on local metal ion concentration measurements. Techniques for such a treatment are more demanding in terms of equipment and operator skill and require further development for effective field use.

No effective method has been achieved for removing the heavy metal precipitates from affected water. In most natural streams diffusion will reduce the esthetic problem and residual toxicity associated with the suspended precipitate so that no significant problem is anticipated if treatment is limited to small spills. More research is required on the eventual fate of the precipitate before conclusions can be drawn relative to the use of this technique on large spills.

Local fire departments throughout the nation can be trained and supplied with the materials and equipment required for applying the sodium sulfide treatment to small heavy metal spills at a very small cost.

4. IMMOBILIZATION OF HAZARDOUS CHEMICALS. Most hazardous chemicals (all tested) spilled on land can be effectively immobilized by the application of the gelling agent formulation developed on this program. This gelling agent consists of equal quantities of four active ingredients, each selected for its ability to congeal one class of chemicals, and one inert powder intended to improve flow and dispersion characteristics. A weight of gelling agent equal to 10 to 25% of that of spilled material is required for complete immobilization.

Surface flow can be stopped by creating dams or levees of congealed material by the application of significantly smaller quantities of the gelling agent to the leading edge of the spill, depending on the nature of the terrain on which the spill occurs. Such a procedure would not inhibit percolation of the spilled material into the soil, however.

Selective use of specific agents for congealing chemicals of the class for which they are applicable could reduce the mass of agent used but would require trained personnel for decision making as to which active ingredient to employ. Once immobilized, the bulk of the congealed material can be removed from the surface by simple mechanical means and placed in suitable containers for shipment or further treatment. Because of the sticky nature of most congealed chemicals, a very small residue always adheres to the surface after mechanical removal and, depending on the nature of the problem, requires further cleanup.

One of the ingredients used in the formulation has excellent lubricating properties even when mixed with large quantities of water and could pose a safety hazard. Care must, therefore, be taken to effect thorough cleanup of the treated area in all regions where pedestrian or automotive traffic is expected.

The gelling agent formulation can be used effectively for sealing long, narrow (e.g., 1/4-inch wide) splits in containers to minimize the quantity of the material that is spilled. In many cases, the specific gelling agents appear to be more effective than the formulation for this purpose. More extensive testing is required.

Gelling can be used very effectively to improve the efficiency of floating booms commonly used to immobilize chemicals that float on water. In most cases booms begin to leak when the thickness of the floating material increases to about 1/16 inch. When the gelling agent is applied to spills of floating chemicals, rafts as thick as 1/4 inch are formed even without booms. Simple booms constructed of lengths of 4" x 4" lumber with a skirt of coarse screen can retain congealed material in floating rafts as thick as four inches without leakage. These thick rafts may be towed across the surface to beaches where the congealed material can be removed mechanically to containers for further shipment.

The cost of the present mix of the gelling agent is approximately \$2.00/lb. Discussions with chemical companies suggest that an equivalent mix could be produced in large quantities at one-fourth that price. Preparations could be made on a national baiss for immobilizing spills with the gelling agent at a cost of under \$10 million.

Many hazardous liquids can be immobilized by absorption in fine powdered material such as fly ash which exists in great quantities in the United States. The use of fly ash to immobilize concentrated sulfuric acid simultaneously provides a mechanical method for controlling reaction rate of the acid with neutralizing agents to prevent excessive bubbling and frothing. This procedure in its crudest form could be used on real spills at its present state of development.

Spills of most heavy metal compounds that have been absorbed by surface soils can be effectively immobilized by treating the soil with sodium sulfide and soaking with water to promote formation of heavy metal sulfide precipitates beneath the surface. These particulates are immobile except in association with land erosion.

Materials that are immiscible with water and are characterized by specific gravity exceeding unit can be effectively trapped beneath flowing water in excavations produced in stream bottoms. The spilled material can then be pumped from the artificial sump into containers on the surface.

5. DETECTION AND MONITORING. Electrical conductivity measurements are effective in detecting the presence and extent of ionic solute spills in water but are not suitable for determining the effectiveness of treatment.

Commercial pH probes and certain specific ion probes are highly effective for detection and measurement of spills of acids, bases and metallic compounds and in monitoring the effectiveness of treatment.

Catalytic combustors are useful for monitoring spills of volatile organic solvents and indicating the potential fire hazard associated with them.

Less volatile organics are effectively observed with multicolor transmissometers.

A cyclic colorimeter which uses modulation of indicator injection to reduce sensitivity to natural turbidity and fouling was designed and tested in the laboratory. Colorimetric indicators are valuable for any spill detection kit.

A spill detection kit containing a conductivity meter, pH indicator, odor samples, and colorimetric reagents was developed and proved effective in tests involving volunteer firemen.

6. MODELING. A mathematical model developed on this program accurately portrays the interaction of activated carbon with phenol in solution under a wide variety of treatment conditions.

The model can be incorporated with a dispersion model to predict effects of treatment and to permit an accurate evaluation of treatment. Simple laboratory experiments can be performed with various carbon-pollutant systems to evaluate constants of the model which will enable the investigator to make quantitative comparisons of activated carbon products.

A small but multifaceted mathematical modeling effort was initiated late in the program. One of the goals of this effort was to investigate the possibility of using desktop computers to obtain useful though primitive solutions to spill dispersion problems as an aid to decision making in the field. A mathematical model was programmed for a Hewlett Packard (Model B-10) computer which, using fundamental physical and chemical properties of the spilled material and estimated dispersion constants, produces graphic printouts of expected concentration isopleths of the spilled material for selected times after the spill.

The value of such a simplified model stems from the ease with which an interaction between the model and real time data acquired at a spill site can be established. Quick comparisons of model predictions with measurements at the spill can be made so that assumed model parameters, such as dispersion coefficients, can be adjusted to be representative of the situation at hand. The model may then be run to provide more realistic predictions of the location and configuration of the spill plume for any desired future times, and thereby permit more realistic decisions to be made relative to the treatment of the spill. In view of the serious uncertainties in values of dispersion coefficients and the wide variations in these values with time and position in a given water body, we believe that only through such an adaptive system can realistic predictions be made.

7. BIOASSAY STUDIES. Toxicity tests were performed with six frequently spilled compounds using fathead minnows, Pimephales promelas, promelas, as subjects. Arranged in order of increasing toxicity to the minnows, they are: methanol, phenol, acrylonitrile, ammonium hydroxide, acetone, cyanohydrin, and chlorine. The bioassay research extended also to studies of the toxicity of the minnows to methods used to treat spilled chemicals, and of the reaction products that may remain in the water after spill treatment.

SECTION 4

RECOMMENDATIONS

1. ACTIVATED CARBON. Three additional investigations are required before extensive preparations are made for implementing the activated carbon treatment procedures developed on this program.

(1) A series of field experiments must be performed to learn how the treatment can best be applied under several types of real conditions, and to provide experience necessary for making realistic decisions relative to implementing large-scale utilization of the procedures. To avoid undue delay, we recommend that the carbon teabag technique be used for these experiments. To properly interpret the data from these experiments and to help in the planning for implementation of the technique, the integrated dispersal-treatment model should be made operational.

(2) A program should be initiated to develop and test a carbon fiber product which has all of the characteristics necessary for treatment of spills. We recommend that the program include the joint efforts of a manufacturing concern such as Carborundum and a corporation having environmental facilities. One goal should be to develop a pilot plant with proper quality control for producing an activated carbon fiber wool with the mechanical and chemical properties of the best sample tested on this program. Production capacity should be sufficient to permit assessment of the product in the field and provide good estimates of large scale production cost. A second goal should be to provide extensive testing of the material, at first to aid in the generation of specifications for the final product and subsequently to provide field experience with its distribution, use and recovery. Small-scale laboratory experiments should be performed with the final product and a wide variety of potential pollutants to generate the constants necessary for use in the treatment model.

(3) A detailed operational analysis should be performed to develop the optimum plan for preparation for, and implementation of, the carbon adsorption treatment procedures for real spills.

2. ION EXCHANGE RESINS. Ion exchange resins are more effective for removal of some pollution from aqueous solutions than activated carbon. A more extensive evaluation than was possible on this program is recommended before decisions are made relative to incorporation of ion exchange resin treatment capability with any activated carbon treatment capability that is implemented.

3. PRECIPITATION OF HEAVY METALS WITH SODIUM SULFIDE. On the basis of the studies of heavy metal spill treatment which have been completed, a number of

recommendations for further action are made. These include a pilot program to verify the suitability of some techniques developed for general spill treatment use, and further studies to refine other techniques and develop them to a state of field utility. Studies are also recommended to improve the environmental effects data base on which treatment decisions must be made.

The basic sulfide treatment process has been proved effective and reasonably safe in laboratory studies and in field-scale experiments. A pilot program should accordingly be undertaken including further field tests and the use of the technique as a response to actual spills and culminating in the distribution of information and materials for spill response to an adequate number of response centers (volunteer fire companies for example are a possibility) to provide rapid treatment of most spills. The program should include a demonstration of the use of the sulfide treatment with a spill tracking kit like that developed in this hazardous spills study which provides for the identification of a variety of hazards.

Further study and development of advanced treatment techniques is recommended to provide low-risk response to large spills. The use of specific-ion electrodes for the metals, the cyclic colorimeter, or a titration and a sulfide electrode to control localized sulfide additions should be studied further. Problems to be solved in achieving effective treatment center primarily on response rate limitations of the detector-human-treatment system and may best be alleviated by development of a more highly automated approach.

Further study of the fate of the sulfide precipitates formed is recommended. A better knowledge of the deposition pattern of the precipitates and of the paths of possible reentry of the heavy metal into the biosphere could provide greater confidence that the spill hazard has been eliminated, or lead to the development of additional spill response procedures.

Finally, the development of a more comprehensive, consistent body of data on the environmental effects of the heavy metals and of treatment materials is considered highly desirable. Attempts to compare hazards and benefits for treatment procedures brought to light a number of deficiencies in existing toxicity data. They were found to be often inconsistent, incompletely reported and reported for a wide variety of organisms (but only a few for any one substance), necessitating cross-species comparisons. It is recommended that toxicity tests be performed for all materials for a few selected test organisms with careful attention to such variables as pH, temperature, and dissolved oxygen and with an adequate control reproducing all factors except the presence of pollutant in the test tank.

4. IMMOBILIZATION OF HAZARDOUS CHEMICALS. The immobilization procedures developed on this program are now ready for experimental use on inadvertent spills, even though significantly more development and testing is required to optimize products, equipment and procedures.

(1) A few organizations with competent, imaginative field personnel should be selected, trained and equipped to apply immobilization procedures experimentally to real spills. Experience obtained

should be documented to aid in the generation of instructions for future use of the procedures. With the assistance of the EPA, authorization should be obtained from local and state authorities to apply these techniques in the field.

(2) The experimental investigation of methods for immobilization of spilled material should be continued and expanded. Emphasis should be placed on developing and testing equipment and techniques for applying the procedures, and on reduction of the hazards, particularly the fire hazards to personnel performing the operations. Techniques should be tested on a larger scale simulating a wider variety of terrain, stream and spill conditions.

(3) Significantly more attention should be given to methods for interrupting a spill by sealing split or punctured containers.

(4) A development program is recommended for optimizing the gelling agent which includes an investigation of compounds which can be substituted one for the other to improve overall effectiveness of the universal blend and provide special features that may be most important for specific areas where special problems exist. Tests should be performed to determine proper particle-size distribution of each component in the mix and the degree of fluidization required for ease of field deployment. The susceptibility to degradation or deterioration under a variety of storage conditions should be investigated. The end product of this effort should be a list of specifications which the EPA could use in a subsequent request for quotation for large quantities of the material for nationwide distribution and stockpiling.

(5) The investigation of the use of ground sealants to prevent percolation was extremely limited on this program because of the inability to acquire proprietary materials. Further investigation is recommended.

(6) A detailed operational analysis is required to determine optimum methods for implementation of the techniques, including distribution of equipment and agents throughout the country, transportation means to spills, operational agencies to be used for treatment, special problems associated with particular regions and educational requirements for operational agencies.

5. PROTECTION OF PERSONNEL. There is a serious need for an investigation of safety precautions to be used by spill cleanup teams. We recommend that such an investigation be initiated immediately. Improved apparatus and procedures should be developed where necessary and recommendations for safe handling of spills should be widely disseminated among the appropriate agencies.

6. DETECTION AND MONITORING. A kit of instruments and chemical indicators similar to the Calspan spill kit should be made available to appropriate federal, state, and local agencies that may be required to respond to spills of hazardous materials.

A short educational movie on the proper use of the kit should be produced and made available to these agencies on a loan basis.

The fact that pH electrodes have been provided with considerable resistance to fouling and other interferences suggests that the same could be done for other specific ion electrodes, e.g., sulfide, bivalent metal, and cyanide probes. Some research and development in this area is in progress. This effort should be encouraged.

Instruments to be incorporated in a device for treating spills of hazardous substances were developed to a point where they could be tested in closed loop control systems. Such tests should be conducted to establish stability and accuracy of this treatment approach. The development of a suitable treatment apparatus was recommended elsewhere.

A fieldable model of the cyclic colorimeter should be constructed and tested under real life conditons at the outfall of a plant where spills may occur.

7. MODELING. The most difficult problem in predicting the location and geometry of a spill plume is the selection of dispersion coefficients that are appropriate to the situation at hand. Additional research is required to obtain sufficient understanding for estimating these coefficients from hydrological information on the different types of water bodies in which spills may occur. We recommend an energetic pursuit of this goal. This effort will necessarily be prolonged and expensive.

As an interim measure, we recommend that attempts be made to test the concept of an adaptive modeling procedure for predicting plume characteristics in a manner similar to that discussed in this report. This effort can be effectively incorporated as part of a field research effort intended to test concepts for cleanup of water spills.

8. BIOASSAY STUDIES. Environmentalists require information on the effect of pollution on complete ecological systems for a variety of purposes involving chronic conditions. Under the practical conditions of an acute spill, which presumably is a one-time event in a given water body, the utility of complete information is mostly limited to the time period devoted to rejuvenation of the water body. The immediate information required for decisions by the director of a cleanup team is the dosage of the spilled material that will produce a significant fish kill. To provide this information, it is recommended that bioassay studies similar to those performed on this program be extended to provide baseline toxicity data for a wide variety of chemicals that may be involved in spills. A single species of moderately tolerant fish, such as the fathead minnow, should be used as subjects in these experiments. Such a program would provide the data necessary for making decisions in the field and simultaneously provide information on the relative toxicities of the important compounds that are most likely to be spilled.

SECTION 5

THE USE OF ACTIVATED CARBON FOR THE REMOVAL OF HAZARDOUS CHEMICALS FROM WATER BODIES

Activated carbon has been used for many years as an adsorbant for organic and inorganic pollutants. It has been used in water treatment plants to remove undesirable odors and tastes from drinking waters, and in recent years, has been used to remove dissolved organics from municipal and industrial wastewater. Because activated carbon is known to adsorb an array of organic substances as well as some inorganic ionic species, it is a logical candidate as a broad spectrum treatment of hazardous organic liquid and heavy metal spills from water.

Early carbon adsorption experiments on this program were aimed at determining the effectiveness of powdered and granular carbons in removing six specific chemical pollutants. The initial objective was to determine dosage requirements for these chemicals, which included methanol, acrylonitrile, acetone cyanohydrin, phenol, chlorine and ammonia. Tests were performed in the laboratory with fixed volumes of solution and continuous, controlled agitation. Pollutant concentrations were measured at prescribed time intervals up to 24 hours. Typical results pertaining to the ultimate adsoprtion capability are illustrated in Figures 1 and 2 where the residual pollutant concentrations after 24 hours of treatment with specific amounts of carbon are plotted.

Various carbon dosages from a ratio of 1:1 to 100:1 carbon-to-pollutant concentration were considered experimentally. Starting with an initial phenol concentration of 1000 ppm, in Figure 1, it can be seen that a 1:1 dosage of carbon to phenol reduces the concentration of phenol about 15%, whereas a 10:1 ratio of carbon to phenol reduces the concentration 95%.

Comparisons of Figures 1 and 2 show that the relative efficiency in terms of total mass of pollutant removed per unit mass of carbon is almost independent of granularity of the carbon used. From Figure 2, it is apparent that for all carbon-to-phenol dosages exceeding approximately 10:1, the residual concentration of pollutant in solution is independent of initial concentrations. The mass of pollutant removed, however, is substantially different. This is best illustrated by replotting the data in the form shown in Figure 3, from which the importance of initiation of the treatment before substantial dilution occurs is readily apparent.

The early experiments showed that generally the ultimate capacity of all of the activated carbon products tested was approximately the same, and that a carbon-to-pollutant ratio of 10:1 is near the optimum for treatment of most organic spills. Table 1 lists examples of a number of different classes of organic components that have been treated with 10x dosages of activated carbon and the percent removal achieved at that dosage. Depending on the nature of the pollutant treated, removal ranged from 48% to 99%. In general, the adsorptive capacity of carbon for an organic pollutant can be related to the solubility, density, polarity, and structure of the organic compound.

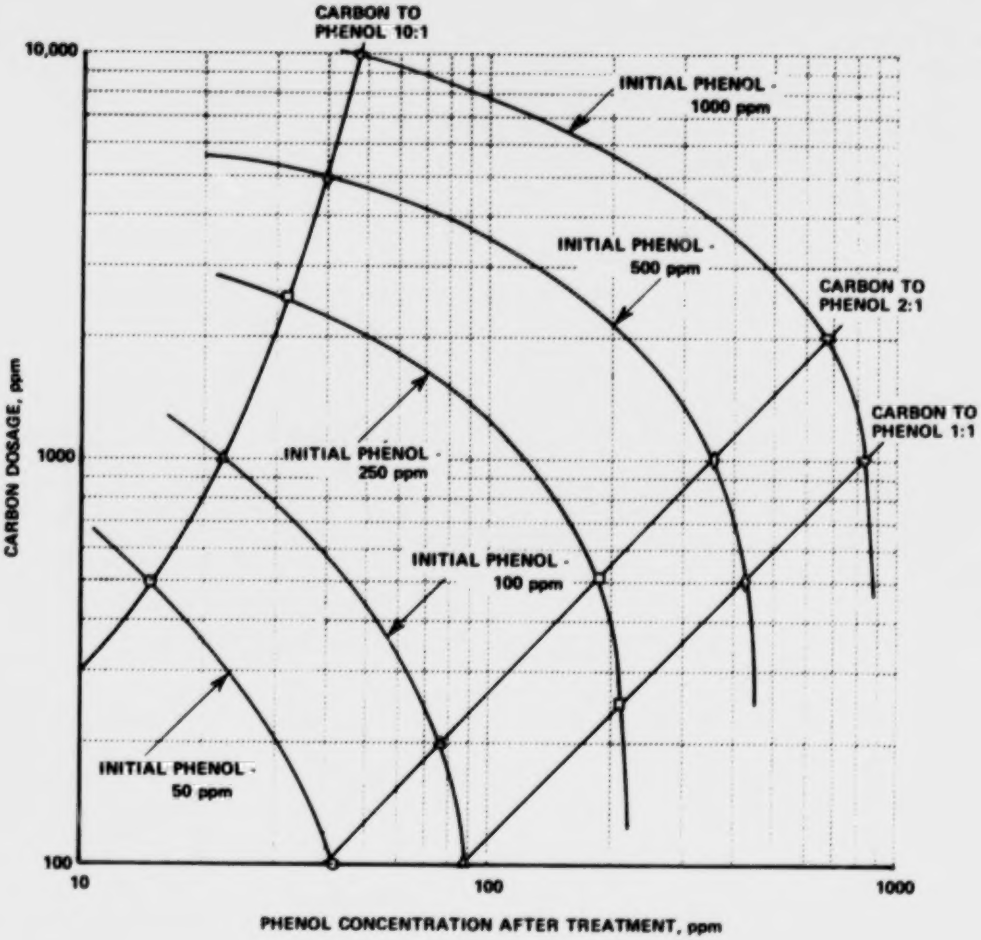


Figure 1 RESIDUAL PHENOL CONCENTRATIONS RESULTING FROM POWDERED CARBON DOSAGES (AQUA NUCHAR A)

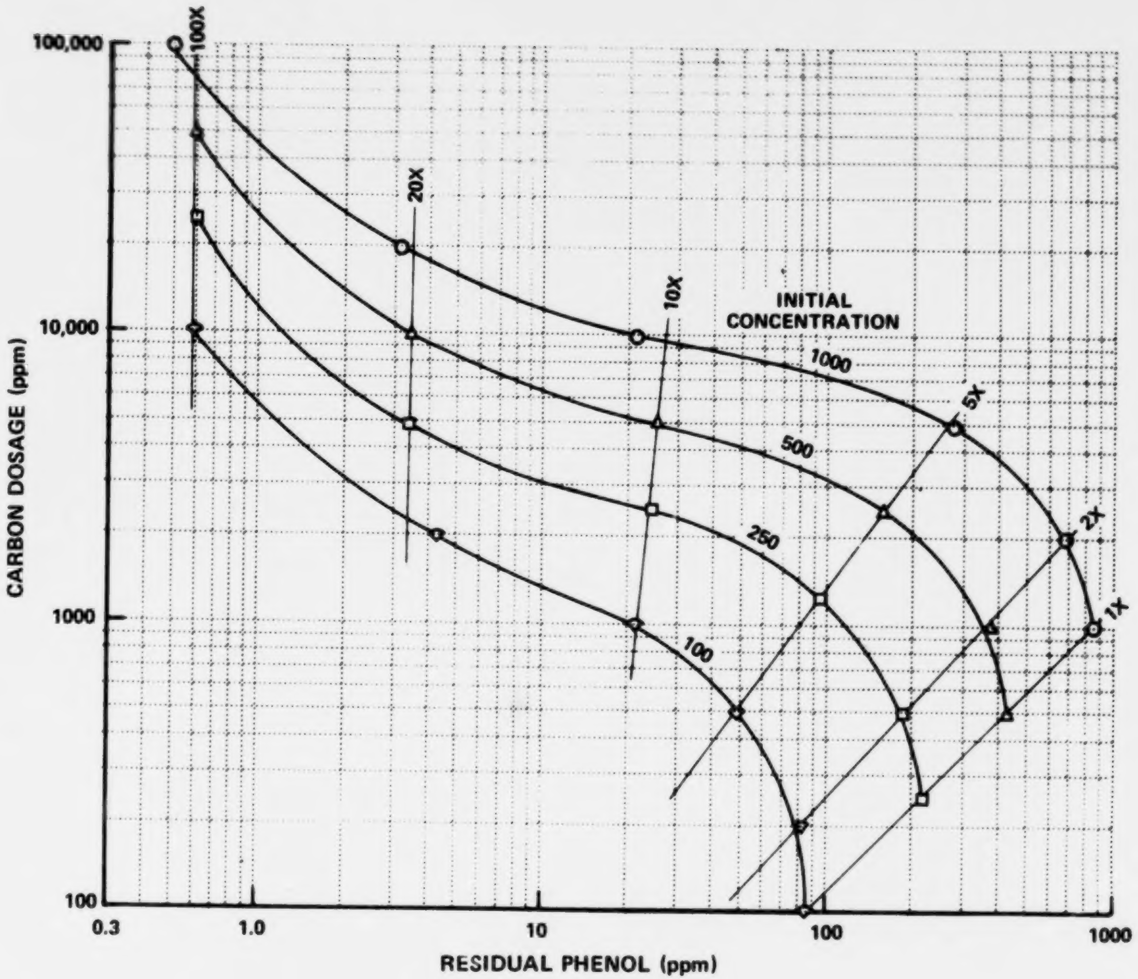


Figure 2 PHENOL REMOVAL BY 8 x 30 NUCHAR UNDER IDEAL CONDITIONS

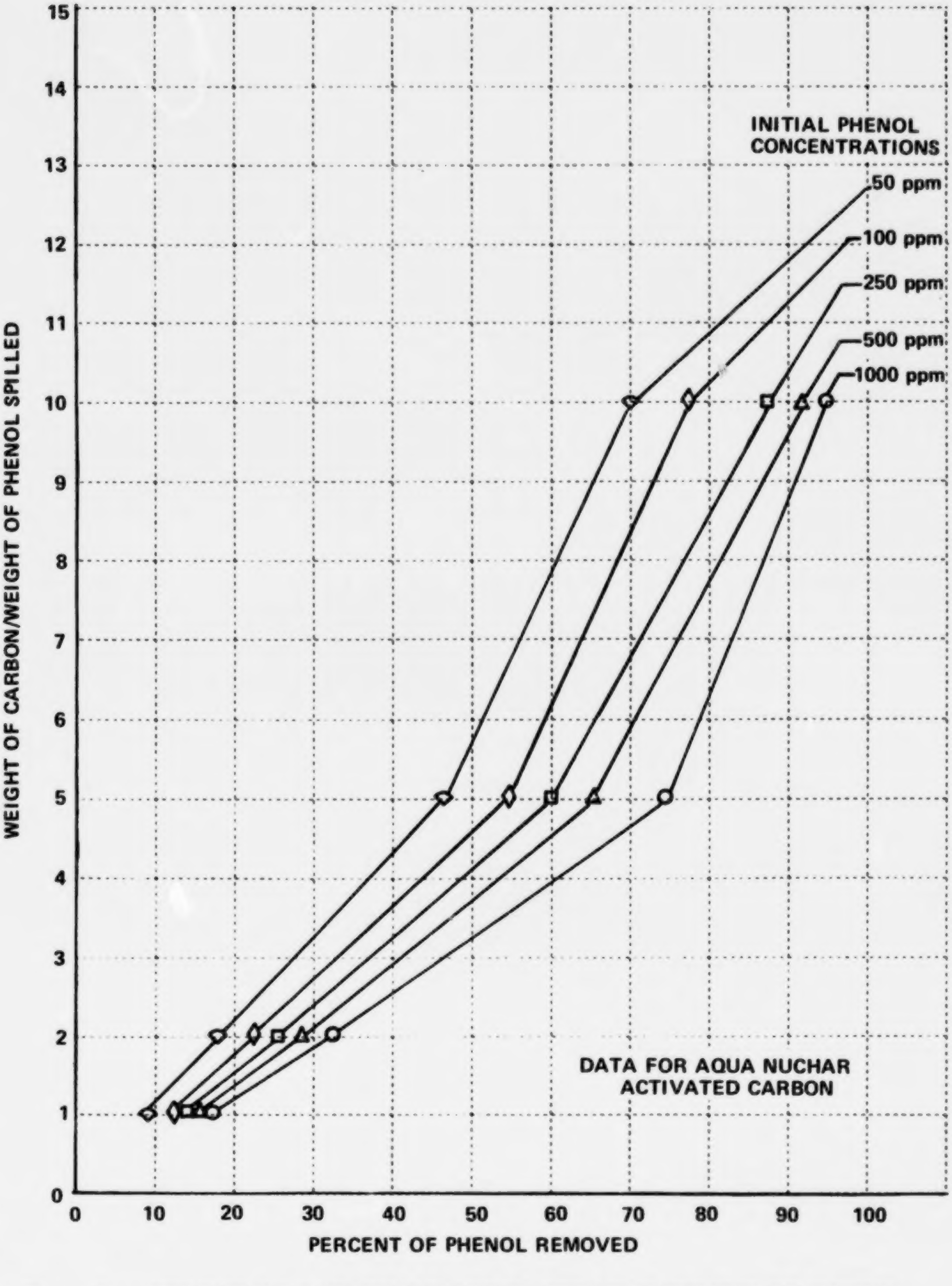


Figure 3 WEIGHT OF CARBON REQUIRED PER UNIT WEIGHT OF PHENOL SPILLED AS A FUNCTION OF PERCENT REMOVAL

TABLE 1
ADSORPTION BY ACTIVATED CARBON

CHEMICAL	INITIAL CONCENTRATION (ppm)	CARBON DOSAGE	RESIDUAL CONCENTRATION (ppm)	PERCENT REMOVAL
PHENOL	1000	10X	3	99
	500	10X	2	99
	100	10X	1	99
ACETONE CYANOHYDRIN	1000	10X	400	60
	200	10X	110	45
	100	10X	70	30
METHANOL	1000	10X	830	17
	200	10X	132	33
	15	10X	10	33
ACRYLONITRILE	1000	10X	490	51
	100	10X	72	28
CHLORINE	1000	10X	0.05	99
	500	10X	0.05	99
	200	10X	0.15	99
	100	10X	0.05	99
PYRIDINE	1000	10X	145	86
	500	10X	71	86
ISOPRENE	1000	10X	110	89
	500	10X	110	78
BUTANOL	1000	10X	249	75
	500	10X	163	67
	100	10X	52	48
BENZALDEHYDE	1000	10X	9	99
	500	10X	6	99
	100	10X	2	98
BENZENE	500	10X	27	95
	250	10X	23	91
	50	10X	20	60
XYLENE	200	10X	29	86
	100	10X	32	68
STYRENE	200	10X	6	97
	100	10X	7	93
	20	10X	9	55

The effectiveness of activated carbon for removal of several inorganic salts from solution has also been investigated. Results are presented in Table 2. It is evident that very high carbon-to-pollutant dosages are required for substantial removal of some soluble metal salts. Required dosages for 50% removal range from 1000x for Cr^{+6} to 5x for Hg^{+2} when initial metal ion concentrations are 100 ppm. It is important to note that mercury, a highly toxic heavy metal, may be very effectively removed from solution by activated carbon. It is also worth noting that lead in the acetate form is also readily removed by this means.

The data in the previously presented figures and tables illustrate the effectiveness of 24-hour treatments with activated carbon. In most cases, 60% to 80% of the reduction of pollutant concentration occurred within the first three hours of treatment; frequently the removal occurred more rapidly. A review of available data confirmed the hypothesis that any treatment procedure which increased contact between the pollutant and the activated carbon increased adsorption rates.

The early experiments demonstrated that the total capacity of activated carbon for many classes of pollutants and the rate of removal of pollutants from water were both consistent with anticipated needs for cleaning spill-contaminated water. Our attention was, therefore, directed toward the development of practical methods for the dispersal of activated carbon in water and the removal of the carbon from the stream or lake after adsorption was complete.

1. POWDERED CARBON. In the laboratory studies, it was shown that the most efficient adsorption is accomplished by powdered carbon in polluted water that is sufficiently turbulent to keep the powder in suspension. However, 1000 ppm of powdered carbon reduced the transparent depth of water to less than 2 millimeters. One percent of that concentration still produced a totally unacceptable turbidity. Addition of flocculents created a thick, unacceptable bottom sludge, and was never more than 99% efficient, leaving turbid water. Bioassay experiments with sludge formed of carbon previously used to remove phenol from water showed some toxicity to fish (50% fatal to fathead minnows in 30 days).

Froth flotation techniques in which compressed air is bubbled through the water in order to float carbon particles to the surface were found to be less efficient than flocculation. Fifty percent recovery of carbon was achieved only with the addition of surface active agents at concentrations which would pose a secondary pollution problem, sometimes equal to the first.

It was concluded, therefore, that free powdered carbon was not suitable for use in natural water, except as a last resort or where the pollutant laden powder would settle to the bottom where it could be located and removed.

2. THE CARBON TEABAG. While granular carbon adsorbs pollutants less rapidly than powdered carbon, its coarse grain size permits greater flexibility in the design of dispersal and retrieval techniques. Among the first concepts considered was a carbon filled porous cloth "teabag." The intial design involved a vertically suspended bag with flotation at its top and well ventilated pockets of activated carbon extending to the desired depth in the water.

Table 2

CARBON ADSORPTION OF Mn, Cu, Ni, Cr, Hg AND Pb

HEAVY METAL TESTED	ACTIVATED CARBON DOSAGE (ppm)	RESIDUAL METAL CONCENTRATION (ppm)	PERCENT REMOVAL	TEST CHEMICAL
Mn^{+2}	0	100	0	$MnCl_2$
Mn^{+2}	500	99	1	
Mn^{+2}	1,000	97	3	
Mn^{+2}	5,000	75	25	
Mn^{+2}	10,000	50	50	
Cu^{+2}	0	50	0	$CuSO_4$
Cu^{+2}	500	46	8	
Cu^{+2}	1,000	45	10	
Cu^{+2}	5,000	13.5	73	
Cu^{+2}	10,000	1.8	96.4	
Ni^{+2}	0	100	0	$NiCl_2$
Ni^{+2}	500	96	4	
Ni^{+2}	1,000	95	5	
Ni^{+2}	5,000	89.5	10.5	
Ni^{+2}	10,000	48	52	
Cr^{+6}	0	100	0	$K_2Cr_2O_7$
Cr^{+6}	500	84	16	
Cr^{+6}	1,000	74	26	
Cr^{+6}	5,000	66	34	
Cr^{+6}	10,000	64	36	
Hg^{+2}	0	100	0	$HgCl_2$
Hg^{+2}	500	1	99	
Hg^{+2}	1,000	1	99	
Hg^{+2}	5,000	1	99	
Hg^{+2}	10,000	1	99	
Cr^{+3}	0	100	0	$CrCl_3$
Cr^{+3}	500	95	5	
Cr^{+3}	1,000	92.5	7.5	
Cr^{+3}	5,000	82.5	17.5	
Cr^{+3}	10,000	52.5	47.5	
Pb^{+2}	0	120	0	$Pb(C_2H_3O_2)_2$
Pb^{+2}	500	49	59.1	
Pb^{+2}	1,000	43	64.2	
Pb^{+2}	10,000	10.5	91.2	
Pb^{+2}	0	107	0	$Pb(NO_3)_2$
Pb^{+2}	500	93	13	
Pb^{+2}	1,000	88	17.7	
Pb^{+2}	5,000	17	84	
Pb^{+2}	10,000	7.5	93	

Considerable design work and testing in stirred beakers resulted in data that are typified by the curves shown in Figure 4. Obviously, the coarse mesh bag with 20 x 50 mesh carbon is most effective, but carbon losses through even fine mesh cloth forced abandonment of the small grain carbon in favor of the more coarse "Nuchar" 8 x 30 carbon, for which losses were less than 1%. This material was used in most of the channel and pool tests described later and appears to be a suitable compromise for use in the field.

Before proceeding to these larger scale tests, a short series of experiments was performed to determine the effect of natural contaminants in water on the removal of spilled material from water. Phenol was used as the test pollutant. As indicated in Figure 5, the variations in water temperature over a range expected in nature have more effect on the rate and extent of adsorption than the type of water involved.

The small-scale experiments described above were followed by a series of tests of the teabag concept under conditions that more nearly simulate natural environments expected in the field. One set of experiments, channel tests, was performed in a 1000-liter, race-track shaped channel 28 feet long, 8 feet wide and having a 1 x 1 foot cross section. Stream velocity through the channel could be controlled between zero and 1.5 ft/sec and bottom roughness could be adjusted by adjusting the distribution of stones placed on the channel bottom. Several teabag configurations were tested with three different types of carbon. Pertinent illustrative data are presented in Figure 6 and compared with standard beaker tests. In all cases, the carbon-to-pollutant ratio was 10:1. The bags were permitted to move freely with the channel water. Ventilation of water through the bags was produced only by the shear and turbulence in the channel.

Comparison of channel Tests 1 and 2 illustrates the importance of bag design and packing. In Test 1, the bags used were constructed with 1-inch wide vertical pockets fully packed with carbon. Without changing other experimental conditions, Test 2 was performed using bags with 1-inch wide horizontal pockets that were half filled with the same carbon. The loose packing permitted less restricted flow of polluted water through the charcoal, which was free to move inside the pockets. The horizontal configuration prevented packing of the charcoal by gravity. Obviously, the Test 2 configuration is superior.

Comparison of Tests 2 and 3 shows that there is no significant effect on removal due to the type of bag fiber provided the mesh size is unchanged and sufficiently coarse to permit flow-through of the contaminated water.

Comparison of Tests 3 and 4 demonstrates the importance of stream velocity in ventilating the carbon in bags. The increased turbulence due to the 1 ft/sec flow velocity in Test 4 caused a significantly increased pollutant removal rate over the rate experienced in Test 3, with a flow velocity of 1/2 ft/sec. This effect is further illustrated by comparison of these results with the "Beaker No Stir" results that are included in the figure. Comparison of channel Test 4 with the "Beaker, Bag Stirred" results suggests that data acquired in our standard beaker experiments may be compared directly with the channel tests performed at 1 ft/sec with loosely packed, horizontally compartmentalized bags.

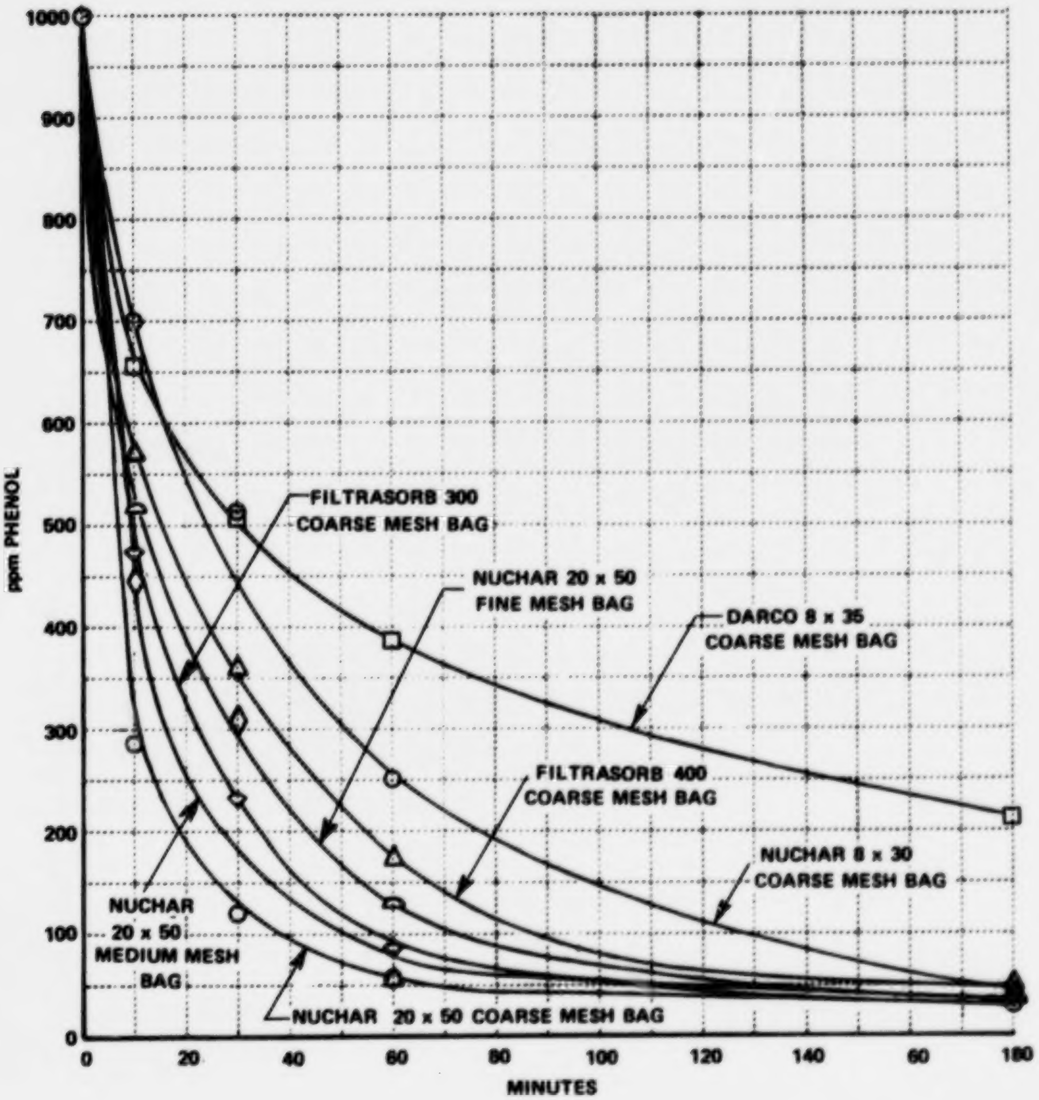


Figure 4 BAG TESTS WITH VARIOUS GRANULAR CARBONS

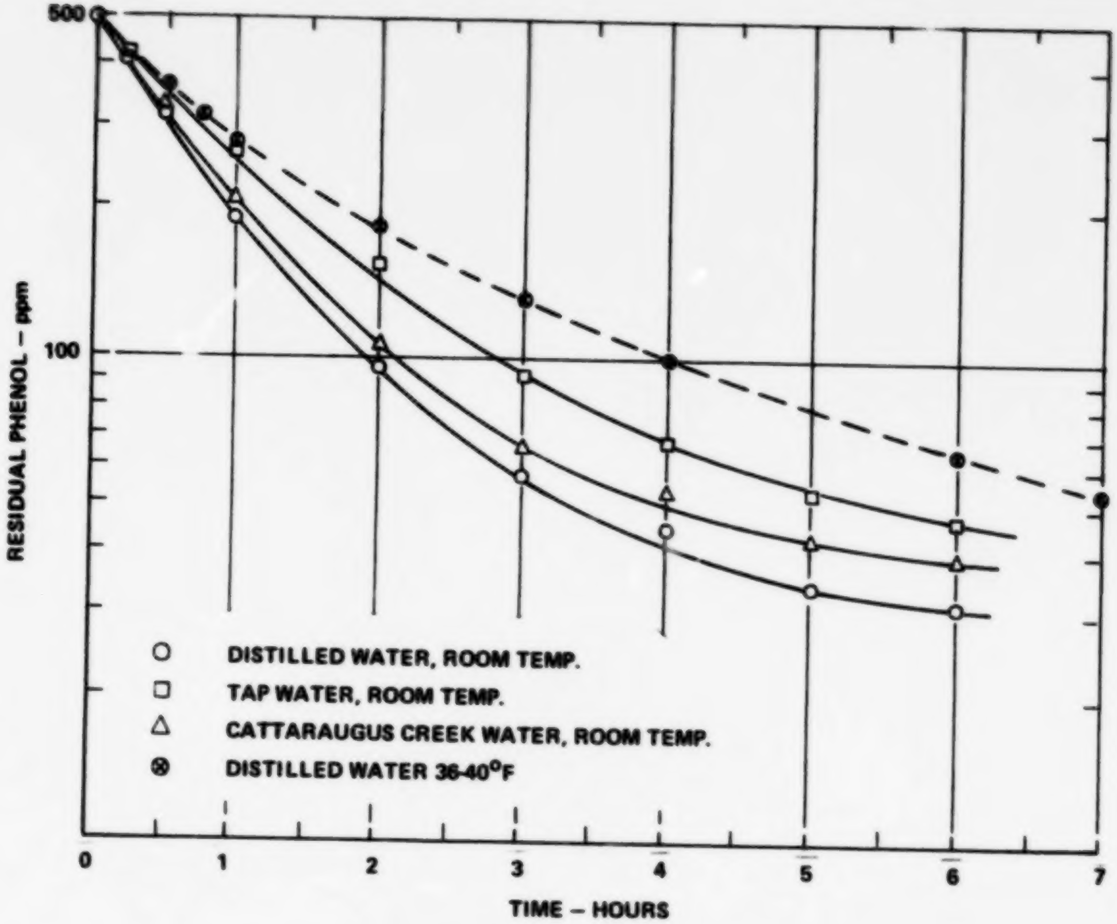


Figure 5 TEA BAG GRANULAR CARBON ADSORPTION OF PHENOL FROM DISTILLED WATER, TAP WATER, AND CREEK WATER

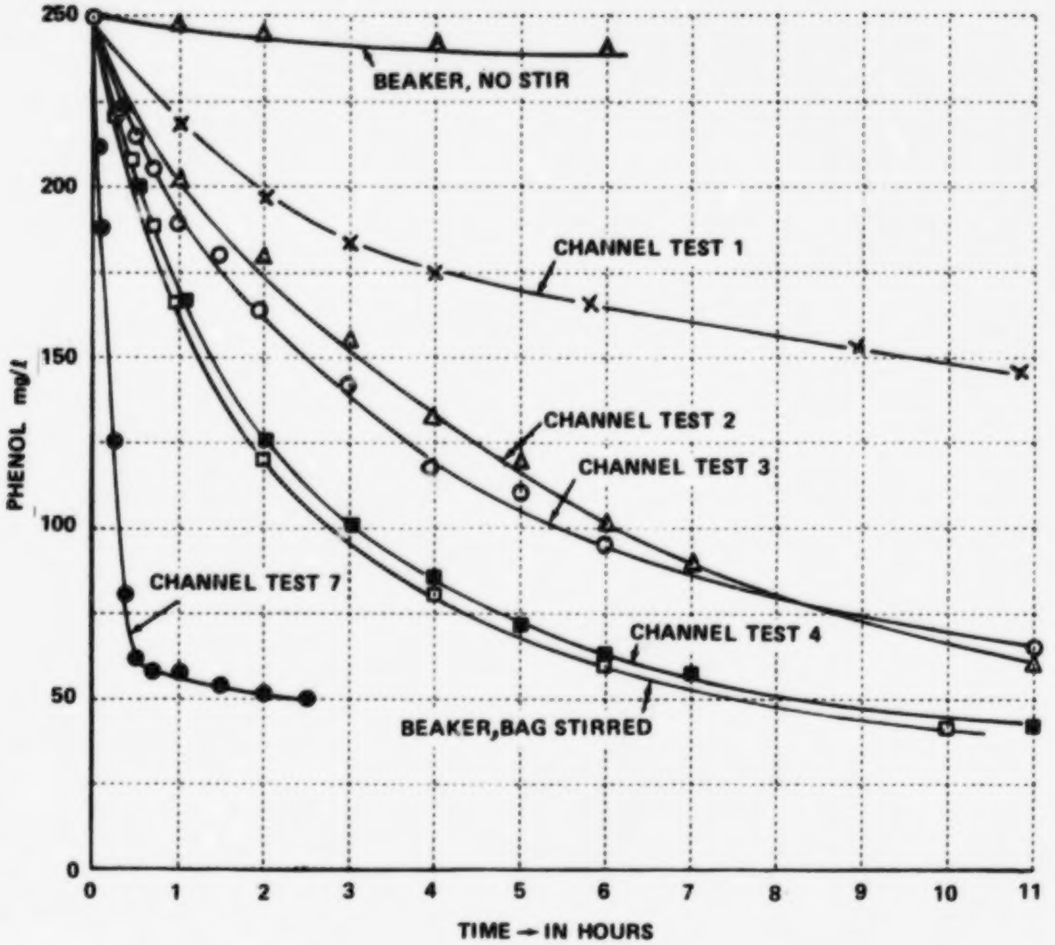


Figure 6 CARBON TEA BAG EFFECTIVENESS UNDER A VARIETY OF CONDITIONS

Channel Test 7 was performed with freely dispersed powdered carbon (Aqua Nuchar A) to provide a baseline against which all other channel tests may be compared.

With the importance of teabag ventilation thoroughly established in these experiments, some concern developed as to the potential value of the concept for treatment of spills that occur in still water such as ponds, lakes, or slow moving streams. A final series of experiments was therefore performed in an outdoor swimming pool, 12 feet in diameter and 3 feet deep filled with 8,000 liters of water. In these tests, we sought to determine if motion associated with waves could provide sufficient ventilation to produce acceptable pollution removal rates. The data are presented in Figure 7 and compared with results of a preliminary wave test performed in the channel.

It is apparent from the "still water" tests that even a small amount of agitation is effective in increasing pollution removal rate. While totally inadequate for effective treatment of spills, the adsorption rate during the first eight hours of the experiment, a period of moderate breeze, was significantly greater than that of the next eight hours during the nocturnal calm. A truly significant increase in adsorption rate resulted from the artificial generation of 2 cm high waves, 40 cm long in the second pool experiment. Similar results were obtained with small artificial waves in the channel under conditions of zero flow. These tests also demonstrated the need for mooring the bags to prevent aggregation and drift due to wave action. A nylon fishing line with fish hooks attached at 1-foot intervals was sufficient to maintain proper separation and position.

This suggests that natural wave action in a lake should be adequate for ventilation of carbon filled teabags. Under very calm water conditions, the waves produced in the wake of a few small outboard motor boats could be used to provide sufficient agitation to permit removal of a significant fraction of spilled material from solution in a few hours.

Schematic drawings of the teabags used in the channel and pool tests are presented in Figures 8 and 9, respectively. The bags were constructed of nylon with thirty threads to the inch to provide a pore size of approximately 0.5 mm. In both cases, each horizontal compartment was filled to one-half capacity with Nuchar 8 x 30 activated carbon to produce a mean loading weight of 30g and 500g per bag, respectively. Either of these configurations could be useful for treatment of spills in natural water, but neither configuration seems applicable for a sufficiently broad class of water bodies.

A design of more general applicability would consist of an arbitrarily long bag (20 to 100 feet) consisting only of carbon-containing compartments similar to those illustrated in Figure 9. Separate flotation units which could be readily attached to the bag at any desired location could be provided to permit adjustment of the depth to which the bag would hang to accommodate the depth of the water body and the nature of the spill. For example, in a 5-foot deep stream, flotation units could be attached every eight feet to permit the bag to hang to the 4-foot level, and just clear the bottom. If the spilled material were

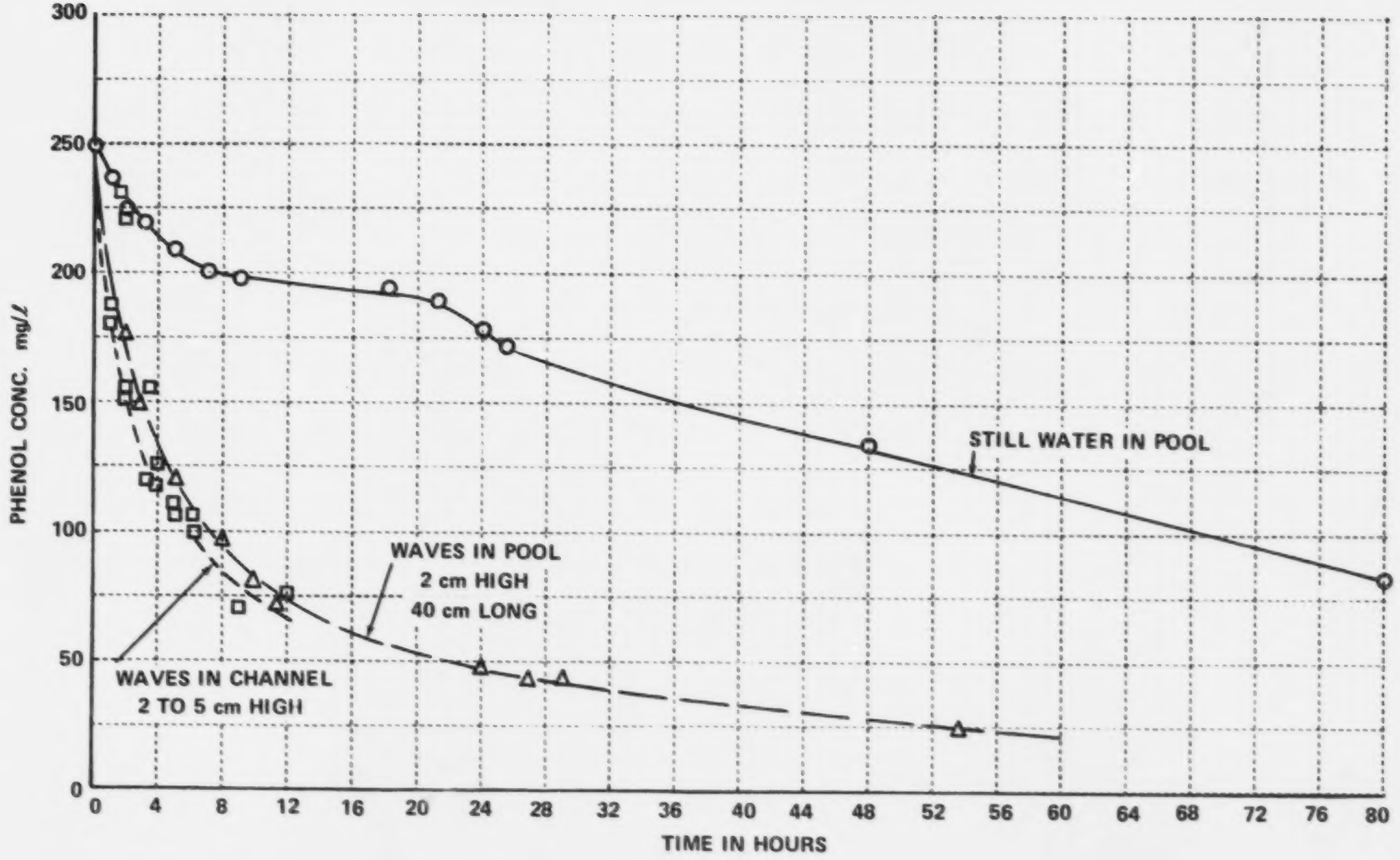


Figure 7 REMOVAL OF PHENOL BY ACTIVATED CARBON (8 x 30 MESH NUCHAR) IN POOL TESTS

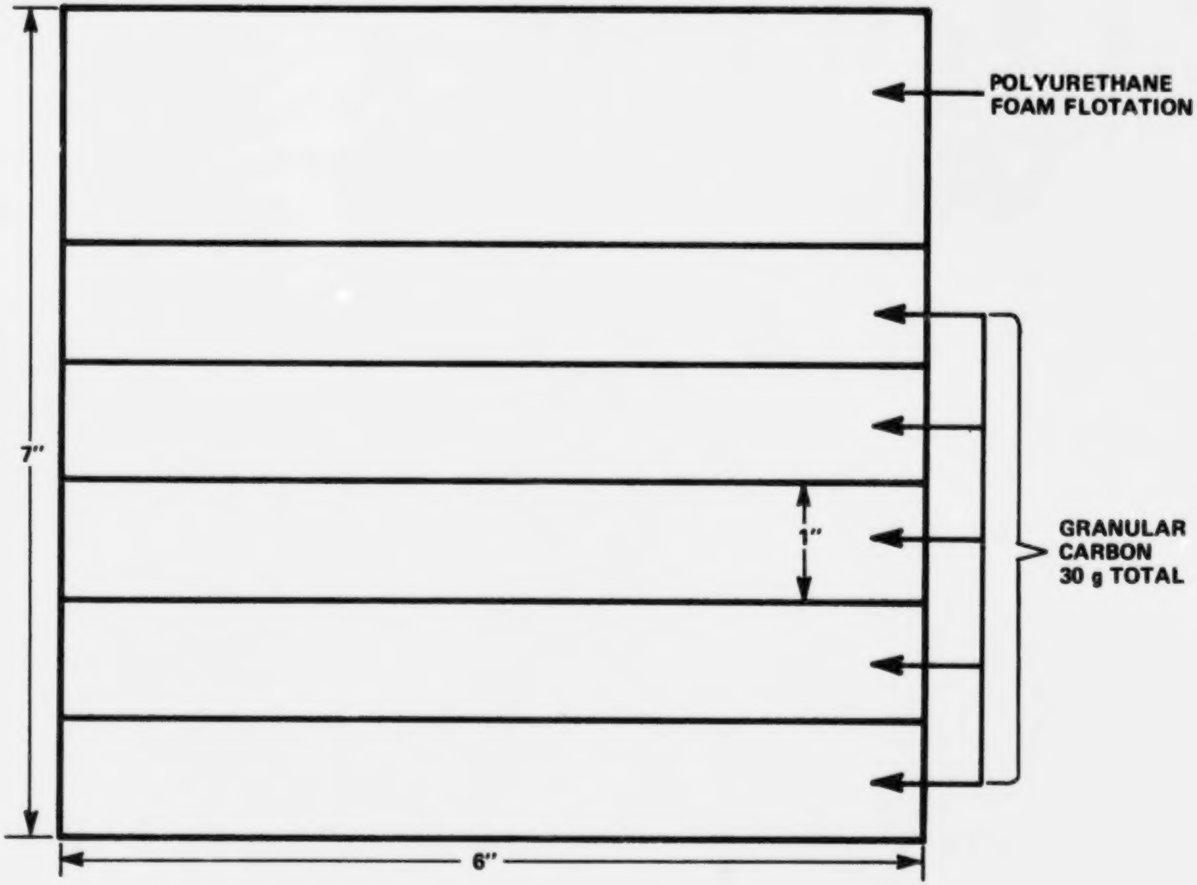

POLYURETHANE FOAM FLOTATION
GRANULAR CARBON 30 g TOTAL
1"
7"
6"

Figure 8 TEA BAG DESIGN, CHANNEL TESTS 2 AND 3

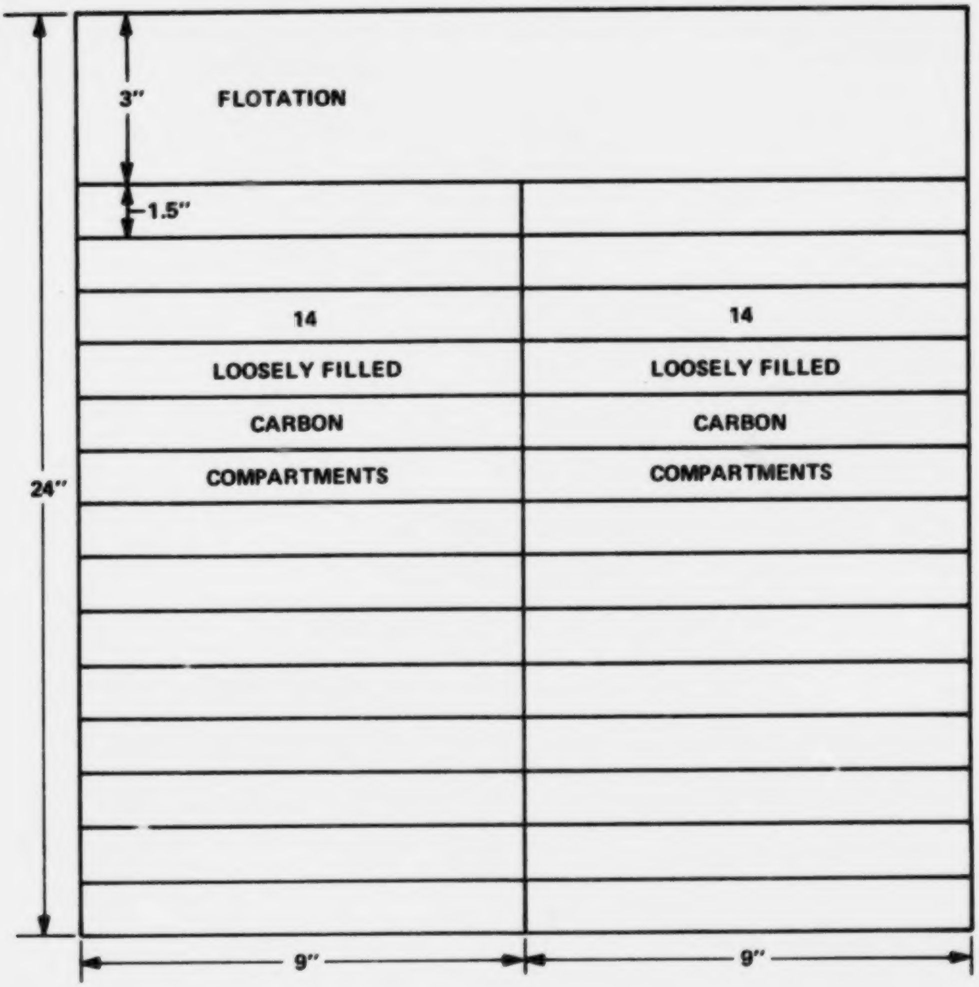

3"
FLOTATION
1.5"
14
LOOSELY FILLED
CARBON
COMPARTMENTS
14
LOOSELY FILLED
CARBON
COMPARTMENTS
24"
9"
9"

Figure 9 TEA BAG CONFIGURATION FOR POOL TEST NUMBER 1

more dense than water and likely to be dissolving from a pool on the stream bottom, the flotation units could be attached at, for example, 15-foot intervals, so that most of the carbon would remain at lower levels where concentration is greatest. Attachment of the units at 2-foot intervals could accommodate spills in shallow water or of materials that are less dense than water and going into solution from floating pools of the concentrated pollutant. While it was impossible to test the effectiveness of this concept in treating a spill or simulated spilled hazardous material, two 10-foot long bags were constructed to evaluate the mechanics of the idea. Tests in the Buffalo harbor indicated that the desired flexibility can be achieved and that the amount of agitation desired from wave action, either natural or artificially produced in the boat wake, would produce the required ventilation.

3. CARBON FIBERS. Recently, several different types of activated carbon filters have become available in small experimental quantities from the Carborundum Company. Beaker tests similar to those for which data are presented in Figure 4 were performed with a variety of these materials to determine their potential for removal of pollutants from water. One variety which resembles loosely packed, fine grain steel wool in appearance shows excellent potential. Test data for this material are compared with channel tests data obtained with freely dispersed powdered carbon in Figure 10. In view of previously discussed results (Figure 6, channel Test 4 compared to Beaker Test, Stirred), we do not consider the difference in test procedure used to be significant

It is apparent from Figure 10 that to within experimental accuracy the carbon fibers are as effective as powdered carbon, both in removal capacity for the test pollutant and in the rate of removal of the pollutant from water.

The wool-like fibers in the tested samples have a density very nearly equal to the density of water. The structural strength of the strongest samples was adequate to permit compression of the matrix for storage and shipment. When placed in water, the matrix expanded almost to its initial configuration and floated with the uppermost fibers at the water surface. Ventilation of the loosely packed fibers, therefore, was excellent. Agitation of this sample did not produce significant fiber fracture. Besides normal stirring, the wool was repeatedly lifted from the beaker with a spatula and replaced without excessive fragmentation. In the field, the material could be readily removed from water using a coarse-mesh net or perhaps a grappling hook.

This steel-wool-like material, therefore, appears to have many of the properties of activated carbon desirable for field use. Other types of carbon fibers tested were either too frangible for consideration or less effective chemically. Since the samples were produced by manual processing on an experimental basis, the variability is quite understandable. Further experimentation and development should be encouraged.

4. OTHER PACKAGING CONCEPTS FOR ACTIVATED CARBON. Two additional concepts were investigated for packaging activated carbon in such a way that it might be retrieved from natural water after treatment was completed. With the aid of the Carborundum Company, activated carbon was bonded to waterproof paper using

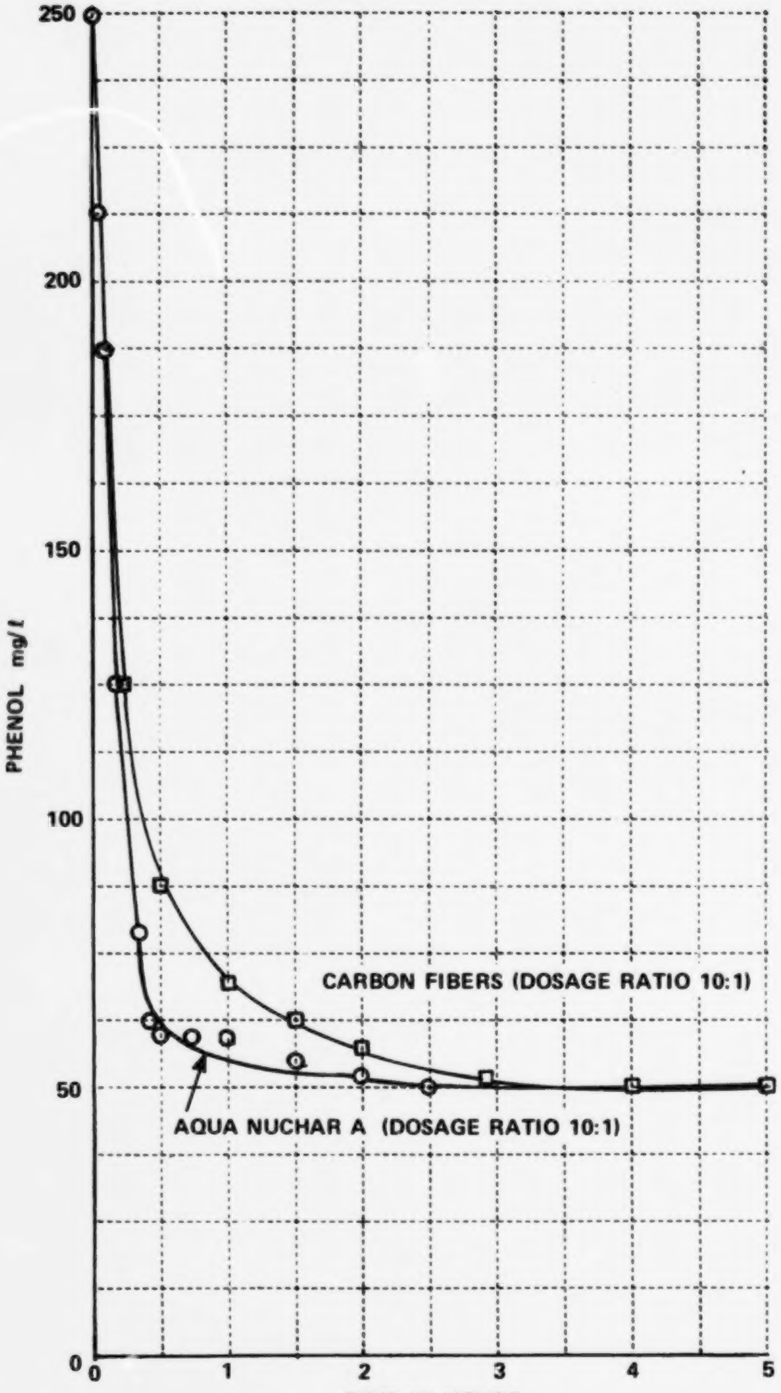


Figure 10 COMPARISON OF CARBON FIBERS WITH POWDERED ACTIVATED CARBON

techniques designed for sandpaper manufacture. Laboratory tests showed that the product was in general less efficient than the carbon filled teabag, primarily because the bonding agent occupied some of the available adsorption sites and restricted access of the pollutant to approximately half of the exterior surface of each carbon grain. Similar results were achieved in in-house attempts to coat reticulated foam with granular carbon.

5. COST AND LOGISTICS. Since the large-scale laboratory and outdoor experiments were not completed until late in this program, extensive analysis of cost and logistic requirements for implementing the teabag concept for activated carbon treatments was not possible. Furthermore, the potential advantages of using the newly developed activated carbon fibers suggest that a vastly superior treatment may become available in the near future. This analysis was, therefore, intended only to determine whether the use of the concept of properly packaged activated carbon showed enough promise of practicability to warrant further development and testing.

The analysis was based on the assumption that 20,000 pounds of properly packaged carbon would be stored at each of 200 locations throughout the United States, and that 100,000 pounds of additional carbon would be stored at each of five Air Force Bases or commercial airports, ready for shipment to any spot in the nation. The purpose of this distribution would be to provide adequate supplies of carbon at "local" warehouses to permit rapid treatment of small spills; i.e., spills of up to 2,000 pounds of material, in a time frame which is consistent with the rate at which the concentration of spilled material is reduced to levels that are too low for effective treatment.

The local supplies would also be available for initiation of the treatment of large spills at about the maximum rate which could be delivered in a very rapid response situation. Even if the 200 caches of carbon were uniformly distributed throughout the contiguous states, there would be 100,000 pounds of material within 120 miles of any spill. The time required to make the decision to treat with carbon, design a specific treatment procedure, and implement the treatment procedure is estimated to be comparable to, or greater than, the time required to transport the carbon 120 miles over land to the spill site (assuming 1 hour for loading, 1 hour for transport of the closest carbon, and 3 hours for transport of the remaining 80,000 lbs from nearby caches).

It was assumed that the first 50 tons of carbon to arrive at a large spill would be dispersed from ten small boats supplied by local agencies (or by local sportsmen to protect their waters). An 18-foot runabout could carry 1,000 pounds of material safely with a crew of three for dispensing the carbon. Assuming 20 minutes for each trip, the 10 boats could disperse the carbon available through ground transportation within four hours after shipment is initiated. The first air shipment of carbon could be available at most sites within that period.

It seems reasonable from a logistics standpoint, therefore, to consider stockpiling 5 million pounds of activated carbon. At the projected price of $2.00/lb, for the carbon, the basic material cost would be $10 million. Packaging might increase this number by 10%.

We have found during the project that granulated activated carbon could be procured and packaged in hand-made teabags for slightly under $1.50/lb. Substantial savings could certainly be effected through automated procedures that could be implemented to fill a large procurement order. The teabag approach to carbon treatment could certainly be implemented, therefore, for under $10 million.

SECTION 6

TREATMENT OF WATER SPILLS WITH ION EXCHANGE RESINS

1. HEAVY METALS. It was shown previously that activated carbon is not effective for the treatment of most heavy metal spills in water. Therefore, laboratory investigations were conducted to assess the relative effectiveness of ion exchange resins (I.E. resins) for the treatment of water spills as compared to activated carbon. Ion exchange resins were investigated for removal of As^{+5}, Cr^{+3}, and Cr^{+6}. Tests were conducted in which ion exchange resin was freely dispersed in water or contained in "tea bags" to facilitate recovery of resin with exchanged pollutants. Parallel tests were run using powdered carbon as the treatment agent to compare effectiveness of carbon and I.E. resin.

The exchange resins used for the experiments were a mixture of cationic and anionic resins normally used for demineralizing of water (Corning No. 3508A). "Tea bags" for holding the resins were made from dacron polyester fabric having a mesh size of 0.4 mm x 0.5 mm.

Test solutions were prepared using sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$), chromium chloride ($CrCl_3 \cdot 6H_2O$), and potassium dichromate ($K_2Cr_2O_7$). Five hundred milliliters of each test solution and one bag containing I.E. resin were placed in each of three beakers and mixed with a magnetic stirrer. Periodically, samples of the solutions were withdrawn and analyzed for residual chromium or arsenic concentration. The results are summarized in Tables 3, 4 and 5.

By comparing removals of arsenic, trivalent and hexavalent chromium by ion exchange resins to removal by activated carbons, it is seen that ion exchange resins, as expected, are much more effective. This is so even when powdered carbon is used and applied loosely, rather than in bags as shown by the chromium data in Tables 4 and 5. For a contact period of one hour using ion exchange resin in tea bags, As^{+5}, Cr^{+3}, and Cr^{+6} removals were 85%, 91.5%, and 97%, respectively. By comparison, removal of As^{+5} by 8 x 30 mesh granular carbon in a tea bag was 5.6% in one hour and removals of Cr^{+3} and Cr^{+6} in one hour using loose powdered carbons were 47.5% and 36%, respectively. Dosages were the same for all treatments (i.e., 10 g/l).

Table 4 indicates the effect which placement of the resins in tea bags has on rate of pollutant removal as compared to free dispersion of the resin in water. Freely dispersed resin resulted in 90% removal of Cr^{+6} in 10 minutes, whereas resin contained in the bag required 40 minutes for an approximately comparable removal of 88%. Containment in bags is desirable, of course, to facilitate removal of the pollutant from the water body after it has been exchanged onto the resin.

Table 3

REMOVAL OF ARSENIC BY ION EXCHANGE RESINS AND ACTIVATED CARBON IN "TEA BAGS"

TARGET POLLUTANT	TYPE, DOSAGE; AND CONDITION OF CHEMICAL AGENT USED	CONTACT TIME Minutes	RESIDUAL CONCENTRATION OF POLLUTANT mg/1	PERCENT REMOVAL
			AS ARSENIC	
ARSENIC Na_2HAsO_4	ION EXCHANGE RESIN (CORNING NO. 3508A) IN A DACRON POLYESTER BAG; DOSAGE = 10 g/1	0	125	0
		5	100	20
		30	73	42
		60	19	85
		240	~ 0	~100
		1440	~ 0	~ 100
	GRANULAR CARBON (NUCHAR 8 X 30) IN A DACRON POLYESTER BAG; DOSAGE = 10 g/1	0	125	0
		5	125	0
		30	122	2.4
		60	118	5.6
		240	105	16.0
		1440	97	22.4
	ION EXCHANGE RESIN (CORNING NO. 3508A) AND GRANULAR CARBON (NUCHAR 8 X 30) IN A DACRON POLYESTER BAG; RESIN DOSAGE = 5 g/1; CARBON DOSAGE = 5 g/1	0	125	0
		5	120	4
		30	86	31.2
		60	30	76.0

Table 4

REMOVAL OF HEXAVALENT CHROMIUM
BY ION EXCHANGE RESINS AND ACTIVATED CARBON

TARGET POLLUTANT	TYPE, DOSAGE; AND CONDITION OF CHEMICAL AGENT USED	CONTACT TIME Minutes	RESIDUAL CONCENTRATION OF POLLUTANT mg/l	PERCENT REMOVAL
HEXAVALENT CHROMIUM $K_2Cr_2O_7$	ION EXCHANGE RESIN (CORNING NO. 3508 A) IN A DACRON POLYESTER BAG; DOSAGE = 10 g/l	0	AS CHROMIUM 100	0
		6	68	32
		10	48	52
		40	12	88
		60	3	97
		120	0.3	99.7
	ION EXCHANGE RESIN (CORNING NO. 3508 A); LOOSE; DOSAGE = 10 g/l	0	100	0
		5	27	73
		10	10	90
		15	4.5	95.5
		20	1.5	98.5
		30	0.8	99.2
		45	0.4	99.6
		60	0.3	99.7
	POWDERED CARBON (NUCHAR C-190N); LOOSE: DOSAGE = 10 g/l	0	100	0
		60	64	36

Table 5

REMOVAL OF TRIVALENT CHROMIUM
BY ION EXCHANGE RESINS AND ACTIVATED CARBON

TARGET POLLUTANT	TYPE, DOSAGE; AND CONDITION OF CHEMICAL AGENT USED	CONTACT TIME Minutes	RESIDUAL CONCENTRATION OF POLLUTANT mg/1	PERCENT REMOVAL
TRIVALENT CHROMIUM $CrCl_3$	ION EXCHANGE RESIN (CORNING NO. 3508A) IN A DACRON POLYESTER BAG; DOSAGE = 10 g/1	0	AS CHROMIUM 100	0
		6	65	35
		10	48.5	51.5
		40	16	84
		60	8.5	91.5
		120	0.5	99.5
	POWDERED CARBON (NUCHAR C-190N); LOOSE; DOSAGE = 10 g/1	0	100	0
		60	52.5	47.5

Treatment of the metals as elemental forms with ion exchange resin required resin to pollutant ratios of 100:1. However, the ion exchange resins used in these experiments consisted of a mixture of both cation and anion I.E. resins. The pollutants (As^{+15}, Cr^{+3}, Cr^{+6}) are all cations. Thus, it is expected that the same percentage removals of metal ions could be achieved with perhaps half as much cation I.E. resin used alone, or a 50:1 treatment to pollutant ratio.

Because carbon treatment was the principal method of spill treatment studied in this project, available resources did not allow for further evaluation of ion exchange "tea bags" in channel or pool tests. In view of experimentation which demonstrated greater removal of some metals with ion exchange resins, further evaluation and development of spill treatment with exchange resins is recommended. An important advantage of resins is that they are easily regenerated for reuse.

2. PHENOL. Phenol removal by both cationic and anionic exchange resins was evaluated in laboratory beaker tests and compared to removal with activated carbon. Exchange resins used were AMBERLITE IR-120-H, a cation exchanger, and AMBERLITE IRA 400-OH, an anionic exchanger. These resins are manufactured by the Rohm and Haas Company.

All treatment agents were applied in loose form at a dosage of 10 g/l. Initial phenol concentrations for all tests were 1000 mg/l. Agitation was provided by magnetic stirring. From the results of these tests, tabulated in Table 6, it is seen that the cation exchange resin does not remove phenol. However, anionic exchange resin, applied loosely, removed a greater amount of phenol than powdered carbon, but does not remove it quite as fast. After five minutes contact, removals of phenol by anion exchanger and powdered carbon were 76% and 97%, respectively. After ten minutes contact, the resin removed almost as much as the powdered carbon. After ten minutes contact, the powdered carbon approached its ultimate capacity for phenol whereas the anion exchange resin continued to remove phenol to the conclusion of the experiment (85 minutes). Granular carbon attained nearly the same removal of phenol as powdered carbon but required nearly an hour more contact time.

The dosage of anion exchange resin as a ratio to initial pollutant concentration in this test was 10:1. On a performance basis then, it would be beneficial to further evaluate anion exchange resins for removal of phenol and substituted phenols which behave similarly in water. Phenol in water behaves as a weak acid and dissociates:

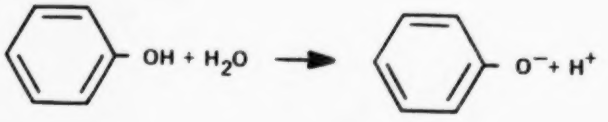
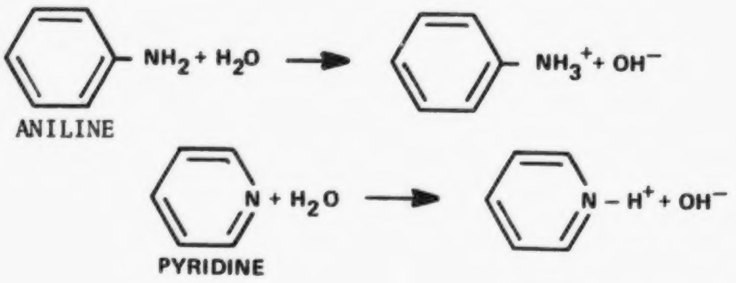


Table 6

REMOVAL OF PHENOL BY ION EXCHANGE RESINS AND ACTIVATED CARBON

TYPE DOSAGE; AND CONDITION OF CHEMICAL AGENT USED	CONTACT TIME Minutes	RESIDUAL CONCENTRATION OF POLLUTANT mg/1	PERCENT REMOVAL
CATION EXCHANGER (AMBERLITE IR-120-H TECH.); LOOSE; DOSAGE = 10 g/1	0	1000	0
	900	1000	0
ANION EXCHANGER (AMBERLITE IRA-400-OH); LOOSE; DOSAGE = 10 g/1	0	1000	0
	1	660	34
	5	240	76
	10	70	93
	60	40	96
	85	6	99.4
POWDERED CARBON (NUCHAR C-190N); LOOSE DOSAGE = 10 g/1	0	1000	0
	5	57.5	94.3
	10	56	94.4
	30	54	94.6
	60	52	94.8
	120	50	95
	180	48	95.2
GRANULAR CARBON (NUCHAR 20 X 50) LOOSE; DOSAGE = 10 g/1	0	1000	0
	5	250	75
	10	140	86
	30	87.5	91.3
	60	65	93.5
	120	45	95.5
	180	42	95.8

The negatively charged ring is exchanged on the anion exchange resin. In a similar manner, a large number of organic amines which are weak bases could be exchanged on cation exchange resins. The dissociation of two widely used organic amine dyes in water, aniline and pyridine, are:



The positively charged rings might be exchanged on cation exchange resins. Available resources did not permit evaluation of ion exchange resins in "tea bags" for organic pollutant removal either in laboratory tests or channel tests. The carload or truckload costs for the anion and cation exchange resins used were $.34/lb and $0.28/lb, respectively. Cost of the 8 x 30 granular carbons used in this research is $0.24/lb while powdered carbon is $0.08/lb. Continued investigation of exchange resins for the treatment of hazardous pollutant spills in water is recommended.

SECTION 7

TREATMENT OF SPILLS OF ACIDS AND BASES BY DIRECT NEUTRALIZATION

Among the hazardous materials singled out for special attention during this project were ammonia, which upon immersion in water forms ammonium hydroxide and chlorine, which reacts with water to form hypochlorous and hydrochloric acids. (The presence of activated carbon which might be added as a countermeasure to such spills in water causes the above reactions to proceed more rapidly and completely to the formation of their end products.)

In addition to these, many other compounds are either acidic or basic in water solutions. These materials may be treated simply by applying stoichiometric amounts of neutralizing weak acids or bases, as appropriate. These less completely ionized agents prevent risking the severe secondary danger of creating adverse pH's by even minor over-treatment or lack of coincidence of the deployed countermeasure with the original spill plume.

Neutralization of alkaline pollutants within two minutes by bubbling of carbon dioxide through the water was demonstrated. Alternatively, neutralization may be achieved immediately upon mixing with acetic acid, a weak acid. It was concluded, however, that the use of carbon dioxide gas will not be cost effective since secondary means of diffusing the gas into the water must be developed to prevent the loss of large quantities of the neutralizing gas to the atmosphere.

Similarly, acidic solutions (especially those containing hydrochloric acid from the interaction of molecular chlorine and water) were readily adjusted to neutral pH with treatments of weak basic substances such as sodium carbonate (washing soda). Neutralizations of acid spills have also been achieved with proper dosages of limewater and aluminum hydroxide.

It was important to determine if these simple neutralization schemes would be applicable in the natural waters which generally are buffered by dissolved substances and biological products at pH's of 7 and above. Using water supplies from different sources (including well water, out-gassed distilled water, water from Cattaraugus Creek, and strongly organic-polluted water from the Buffalo River) which ranged in initial pH from pH 7 through pH 8.3, the above-stated conclusions were confirmed experimentally. In no instance was it found that significant deviations from simple stoichiometric neutralization occurred. With weak acid and weak base countermeasures, a very large region of pH "forgiveness" was found, without apparent influence from the initial pH of the water into which the spill occurred or of the presence or absence of adventitious buffering substances in the initial water supply. Thus, the use of weak acid and weak base countermeasures to their appropriate base and acid spills, respectively, can be recommended.

As is true for any large spill, it will be difficult to estimate the exact amount of spilled material that actually reaches the water or the distribution of that material in the water. With large spills of both acidic and basic materials, it seems particularly appropriate to utilize an automatic treatment device of the type recommended on page 49 of this report. The neutralization of acidic or basic materials spilled directly onto the ground was studied during the large scale demonstration phase at Calspan's Bethany, New York site. This experiment in which concentrated sulfuric acid was neutralized with lime is described in Section 9.

SECTION 8

PRECIPITATION OF HEAVY METALS WITH SODIUM SULFIDE

The treatment of spills of soluble heavy metal compounds, by precipitation of the generally insoluble metal sulfides, was evaluated as part of the project. The technique is potentially useful for many materials and was found to be effective in treating solutions of most of the heavy metal compounds which present a spill hazard. It was shown to be simple to apply and capable of reducing the toxic hazard presented by heavy metal ions in solution.

The treatment is applied by introducing sulfide ions, derived from a solution of sodium sulfide, into the spill. At concentrations of the heavy metal ion that present a toxic hazard, formation of the sulfide precipitate proceeds rapidly, and toxicity is reduced within seconds. The treatment chemical is stabilized by the addition of some sodium hydroxide, in order to prevent evolution of toxic hydrogen sulfide fumes.

In the case of small spills, that are typical of the majority of heavy metal spills reported in the past two years, treatment can be applied on the basis of a simple test: A small amount of sodium sulfide (Na_2S) is injected at the spill site. If a visible precipitate forms, additional treatment material is applied until about one-half gallon (4 liters per kilogram) of concentrated Na_2S solution is used for every pound of spilled material. For larger spills this process may result in inadequate treatment and more exact procedures are advocated.

A wide range of heavy metal compounds can be treated by the sulfide method. Since several thousand compounds should be considered, a detailed listing of these compounds of the metals indicated by a slash mark in Table 7 are subject to sulfide treatment because the sulfide is their least soluble compound whenever excess sulfide ions are available. To demonstrate the effectiveness of sulfide treatment, soluble compounds of the commercially important metals listed in Table 8 were investigated. Sulfide treatment was found to be unsuitable for spills of two groups of heavy metals. (For the sake of brevity, the term "metal" is used for the ions generated by solution of a compound in the following. Bulk elemental heavy metals, if spilled, can usually be recovered before they present a noticeable toxic hazard to waterways.)

In the first instance there are those which, like titanium and aluminum, have greater affinity with oxygen than sulfur and whose reactive compounds hydrolyze in the presence of sulfide ion to form hydroxides and oxides. These often require no treatment, as they are quickly precipitated by mere contact with natural water. A second problem arises in the treatment of high oxidation states, chromium, molybdenum, manganese, vanadium, and tungsten, that cause the metal to be presented in anionic species, e.g., as the chromate, molybdate, or permanganate, etc. Sodium sulfide is often effective in reducing such species to a lower valence from which precipitation, usually as a hydroxide,

Table 7

PERIODIC TABLE OF THE ELEMENTS

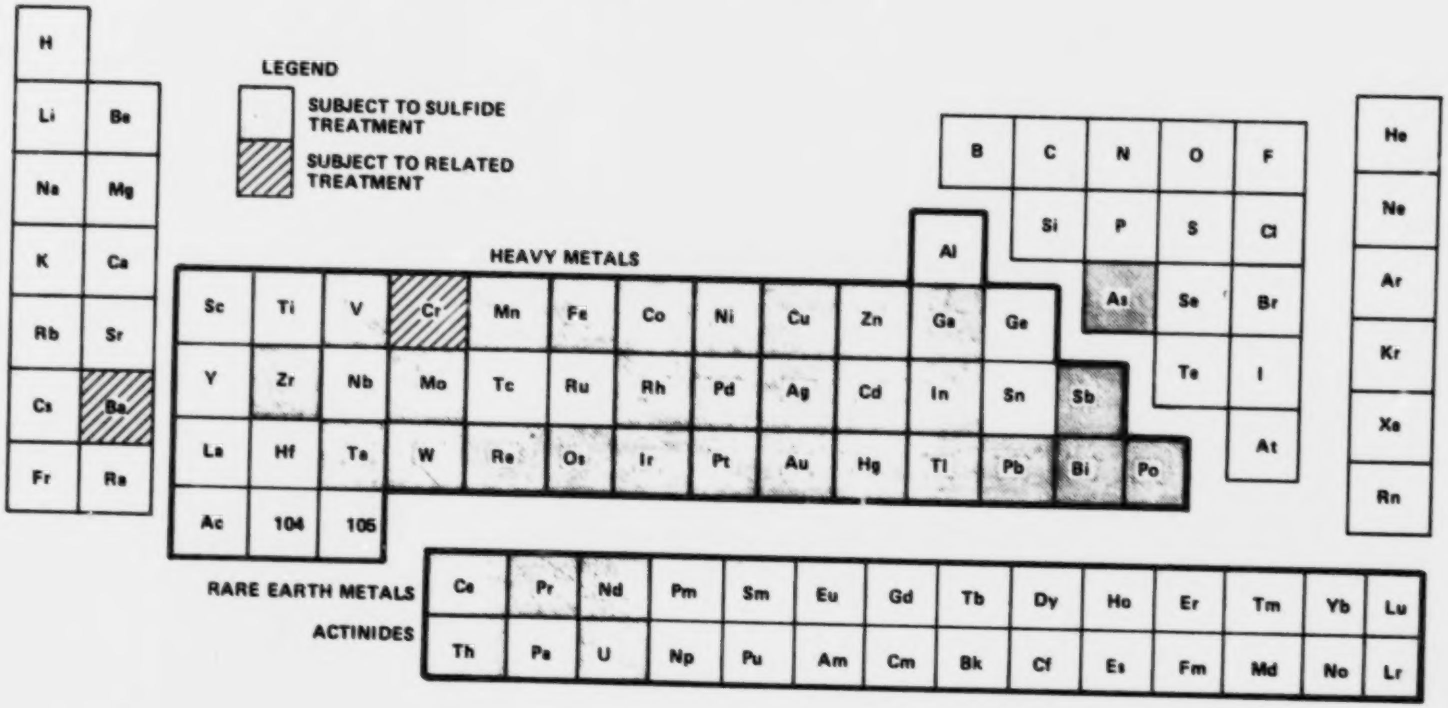

LEGEND
SUBJECT TO SULFIDE TREATMENT
SUBJECT TO RELATED TREATMENT
HEAVY METALS
RARE EARTH METALS
ACTINIDES
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Ac 104 105
Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

Table 8

QUANTITY OF STANDARD SULFIDE TREATMENT*
SOLUTION REQUIRED TO TREAT ONE POUND SPILLS
OF INDICATED COMPOUNDS

COMPOUND	FORMULA	TREATMENT
SILVER NITRATE	$AgNO_3$	0.270 gal
CADMIUM CHLORIDE	$CdCl_2$	0.500 gal
COBALT CHLORIDE	$CoCl_2$	0.706 gal
COBALT CHLORIDE	$CoCl_2 \cdot 6H_2O$	0.385 gal
COPPER SULFATE	Cu_2SO_4	0.411 gal
COPPER SULFATE	$CuSO_4$	0.575 gal
COPPER SULFATE	$CuSO_4 \cdot 5H_2O$	0.367 gal
IRON SULFATE	$FeSO_4 \cdot H_2O$	0.540 gal
IRON SULFATE	$FeSO_4 \cdot 4H_2O$	0.409 gal
IRON SULFATE	$FeSO_4 \cdot 7H_2O$	0.330 gal
IRON CHLORIDE	$FeCl_3$	0.848 gal
IRON CHLORIDE	$FeCl_3 \cdot 6H_2O$	0.509 gal
MERCURY CHLORIDE	$HgCl_2$	0.338 gal
MANGANESE SULFATE	$MnSO_4$	0.607 gal
MANGANESE SULFATE	$MnSO_4 \cdot H_2O$	0.543 gal
MANGANESE SULFATE	$MnSO_4 \cdot 2H_2O$	0.490 gal
MANGANESE SULFATE	$MnSO_4 \cdot 3H_2O$	0.447 gal
MANGANESE SULFATE	$MnSO_4 \cdot 4H_2O$	0.411 gal
MANGANESE SULFATE	$MnSO_4 \cdot 5H_2O$	0.380 gal
MANGANESE SULFATE	$MnSO_4 \cdot 6H_2O$	0.354 gal

*0.851 lb Na_2S and 0.040 lb NaOH per gallon H_2O.

Table 8 (Cont.)

COMPOUND	FORMULA	TREATMENT
MANGANESE SULFATE	$MnSO_4 \cdot 7H_2O$	0.331 gal
NICKEL SULFATE	$NiSO_4$	0.593 gal
NICKEL SULFATE	$NiSO_4 \cdot 6H_2O$	0.349 gal
NICKEL SULFATE	$NiSO_4 \cdot 7H_2O$	0.326 gal
LEAD ACETATE	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$	0.242 gal
LEAD ACETATE	$Pb(C_2H_3O_2)_2 \cdot 10H_2O$	0.181 gal
ZINC CHLORIDE	$ZnCl_2$	0.673 gal
ZINC SULFATE	$ZnSO_4 \cdot 7H_2O$	0.319 gal

is possible. This process is often accompanied by the evolution of hydrogen sulfide and is not recommended. Alternate methods for the treatment of chromate and dichromate spills, which are quite common, have been investigated. Barium compounds are produced in quantity, and although barium is not subject to sulfide treatment, its fate in case of spills was considered. The carbonate and particularly the sulfate of barium are sufficiently insoluble that spills of moderate quantities of soluble barium compounds should quickly precipitate in natural bodies of water containing their salts.

The correct treatment of a metal spill requires application of sulfide treatment in a definite (stoichiometric) ratio that assures that each metal ion combines with an appropriate number of sulfide ions to yield the insoluble sulfide. Most of the commercial metals are bivalent, as is sulfur, and each metal ion combines with one sulfide ion. It is also found that the atomic weights of metals treatable by the sulfide method occur in groups centered on 60, 105, and 200, and that the lowest group (ranging from 55 for Mn to 65 for Zn) contains the commercially important elements manganese, iron, cobalt, nickel, copper, and zinc. Each pound of the ions of these metals requires about 1.3 pounds of sodium sulfide for complete conversion to the insoluble sulfide. Unfortunately, the metals are encountered as compounds with various anions and with water of hydration. Because of these, the ratio of sodium sulfide treatment, in the form of a concentrated (at 0°C) solution needed to treat a one-pound spill, varies from 0.181 gallons for lead acetate to 0.848 gallons for ferric chloride.

Some method of estimating the quantity of treatment to be applied to a spill is needed when the amount or kind of material spilled is not known. The use of specific ion electrodes for the metals or for the sulfide ion itself was investigated in a spill simulation facility, using iron as a heavy metal. The flow conditions dictated a frequency of sulfide additions of at least one every ten seconds. The required operations (reading the specific ion meter, determining sulfide addition, and making the addition) proved too complex for all manual operation on this time scale, and the treatment achieved was far from ideal. The iron concentration was nonetheless substantially reduced. Residual iron in this case was estimated to be less than 16 mg out of 520 mg added in the original spill. This is to be compared to a residue of 7 mg out of 520 mg when the exactly stoichiometric treatment was applied. The use of specific ion electrodes for the metals, the cyclic colorimeter, or of a titration and a sulfide electrode, to control localized sulfide additions should be studied further. Problems to be solved in achieving effective treatment center primarily on response rate limitations of the detector-human-treatment system and may best be alleviated by the development of a more highly automated approach.

In order to evaluate automated spill treatment procedures, an apparatus whose general features are shown in Figure 11 could be used. The device could be used for sulfide treatment of heavy metal spills as well as for acid-base neutralization which follows similar rules. It utilizes direct control of treatment and feedback to compensate for errors in measurement and would permit design of a stable treatment control system.

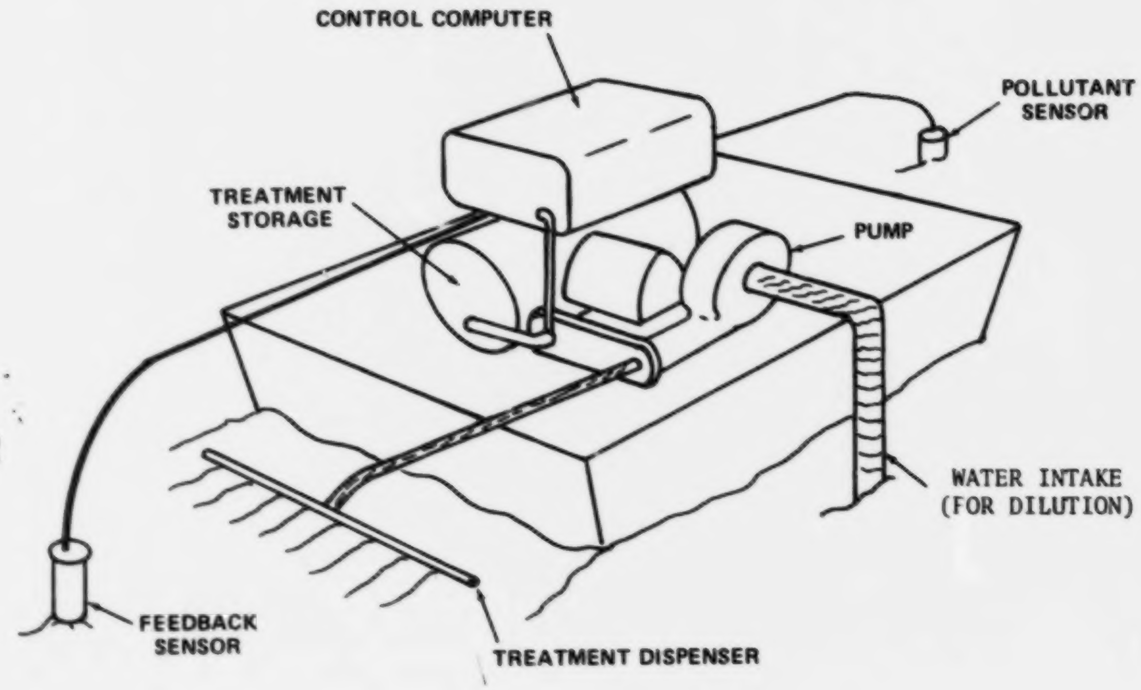

CONTROL COMPUTER
POLLUTANT SENSOR
TREATMENT STORAGE
PUMP
WATER INTAKE (FOR DILUTION)
FEEDBACK SENSOR
TREATMENT DISPENSER

Figure 11 LARGE SPILL TREATMENT BARGE

Sulfide precipitation has been shown to be effective in significantly reducing the levels of heavy metal ions in solution and thus reducing the toxic hazard of a heavy metal spill. In the process, however, sodium sulfide, a material which is itself toxic, is introduced into the environment. It is important therefore to assess the hazards posed by this material and to compare them to the benefits to be derived from its use. The preparation of a completely satisfactory comparison between the hazards and benefits of the sulfide precipitation treatment of heavy metal spills would require a significantly greater body of data than that available at this time. Ideally the spreading of plumes of heavy metals and sodium sulfide over a range of stream conditions should be correlated with complete toxicity-concentration-exposure time data for these materials to compare the environmental damage caused by untreated spills, treated spills, and erroneous treatment where there was no spill. In this study a much less rigorous approach has, by necessity, been taken. One can make a rudimentary comparison between the consequences of not treating a heavy metal spill and the consequences of applying sodium sulfide treatment where no spill had occurred. The comparison is made in terms of the volume of water contaminated at a level lethal to fish. Despite the crude nature of these comparisons, it is felt that the differences between the metal spill results and the sulfide "spill" results are sufficiently great to support the conclusion that sulfide treatment should be recommended for heavy metal spills, with some reservations, as outlined below.

The hazard involved in treating a nonexistent spill or of mistreating a spill clearly depends on the amount of material released to the environment. Experience has shown that heavy metal spills typically involve small quantities, of the order of a few kilograms. For comparison of effects, a spill of 4 kg of each heavy metal compound for which toxicity data corresponds to data available for the sulfide is taken as an example. The volume of water which could be contaminated to the reported lethal level by such a spill was calculated. A comparison of these two volumes (Table 9) corresponding to no treatment and to the worst possible treatment action provides a measure of the benefits and hazards of sulfide treatment.

The ratios of the affected volumes vary widely, even with different data for the same heavy metal, but in no case is the sodium sulfide toxic in more than 5% of the volume calculated as lethal for the heavy metal. Further, it may be seen that the affected volume is quite small for all the sodium sulfide additions, even in the case of $ZnSO_4$ treatment where the greatest amount is added, and the sulfide toxicity corresponds only to 10% fish mortality in seven days. The hazard occasioned by sodium sulfide is further alleviated by the instability of the sulfide ions in the environment which was not accurately reproduced in the laboratory toxicity tests where contact with water of lower pH than that of the Na_2S solution did not occur.

The acute toxicity of sodium sulfide solutions in various concentrations was measured and compared with the toxicity of sodium hydroxide. Both sodium sulfide and hydroxide raise the pH of their aqueous solutions and this alone may occasion some toxicity. Figure 12 shows 24-hour toxicity versus concentration of these compounds (in mg of compound per liter) while Figure 13 shows

Table 9

COMPARISON OF HEAVY METAL AND Na_2S HAZARDS

HEAVY METAL COMPOUND	AMOUNT Na_2S TO TREAT 4 kg	WATER CONTAMINATED BY HEAVY METAL	WATER CONTAMINATED BY Na_2S
$CdCl_2$	1.75 kg	150,000 m^3	22 m^3
$CdCl_2$	1.75	400	18
$CdCl_2$	1.75	240	12
$CuSO_4$	1.25	3,300	30
$HgCl_2$	1.20	300	9
$HgCl_2$	1.20	30,000	10
$Ni(NO_3)_2$	1.15	800	30
$Pb(NO_3)_2$	0.9	12,000	25
$ZnSO_4$	2.0	13,000	50
$ZnSO_4$	2.0	8,000	50

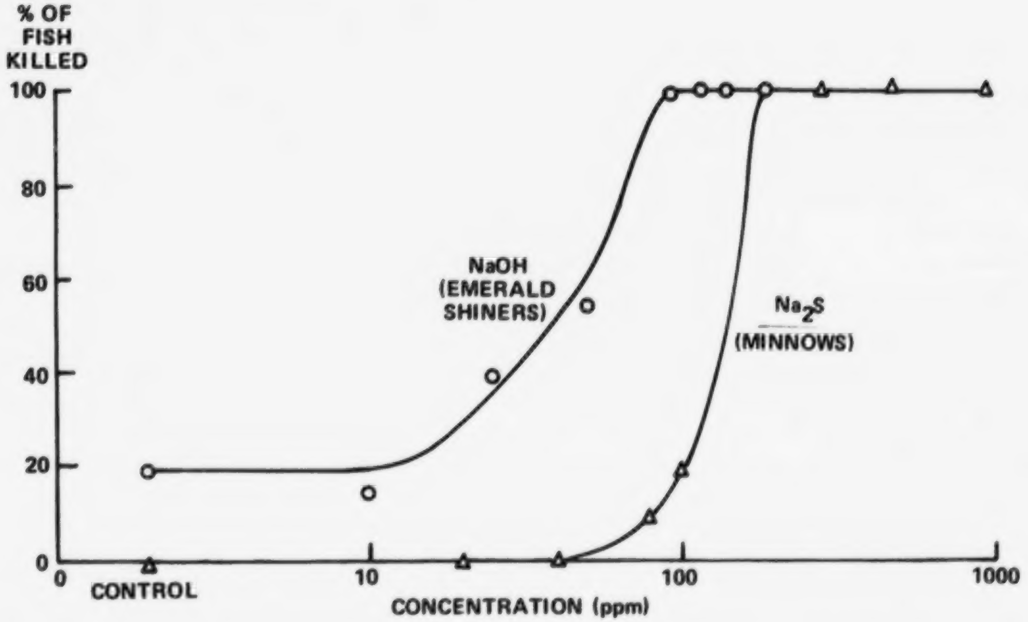


Figure 12 TOXICITY OF Na_2S AND NaOH (24 HOUR EXPOSURE)

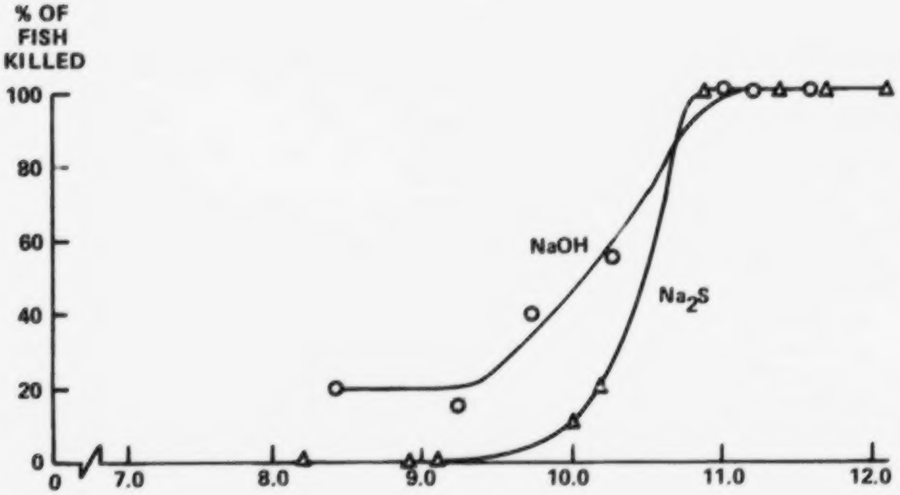


Figure 13 TOXICITY OF Na_2S AND NaOH AS FUNCTIONS OF pH OF THEIR SOLUTIONS (24 HOUR EXPOSURE)

the same toxicity as a function of pH. The pH is closely related to the molar concentration of the compounds and Figure 16 indicates that there is relatively little difference between the molar toxicity of sodium sulfide and hydroxide.

Many pollutants ultimately leave the environment by conversion to useful or at least acceptable chemicals. For example, both chemical and biological processes tend to oxidize most organics to water and carbon dioxide. Metals differ in this respect; those metals whose ions are toxic will continue to pose a threat indefinitely if they are not rendered insoluble and stored in an environment which inhibits redissolution. The sulfide precipitation treatment was shown to be effective in rendering many heavy metal ions insoluble. Collection of the precipitate and return of the heavy metal content to commercial channels proved to be impractical in some cases. When the sulfide precipitate is released into the environment, it may undergo slow redissolution because its solubility product is finite. Ultimately the heavy metal is converted to the least soluble species for which anions are available.

In well-aerated surface water the hydroxyde (OH) ion is most available and hydroxides are commonly formed from available metal ions. These precipitate to greater depth in the oceans, eventually encountering a reducing environment where excess sulfide ion exists. In this environment, stable deposits of heavy metal sulfides are formed in sediments.* It is believed that the processes at the interface between the anaerobic interior of sediments and the aerobic water in shallow, well-agitated waterways are similar. One may, therefore, assume that heavy metal sulfides are immobilized once they are included in a stable sediment. The organic nature of bacteria may lead to feedback, however, and this feature was investigated separately.

Several experiments were conducted to investigate the environmental effects of sulfide precipitates remaining in the environment. A series of experiments were run in which minnows were exposed to the metal sulfides individually for periods of 60 days. No significant evidence of toxicity of the sulfides of zinc, copper, lead, cadmium, or manganese was found in these tests. In the tanks containing CoS and NiS, 20% and nearly 60%, respectively, of the fish died within 60 days as compared with 5% mortality in the control tank. Maximum concentrations of dissolved ion in these tanks were 7.0 ppm Co and 8.0 ppm Ni. Significantly more fish died in the tank containing silver sulfide than in the control also, but no dissolved silver was ever detected so the reason for this result is not clear.

One further experiment was conducted as a preliminary investigation of the reentry of heavy metals into the biosphere following sulfide precipitation. A simple ecosystem was established in a tank carpeted with a sediment made up of kaolin, and two grams each of the sulfides of silver, cadmium, cobalt, copper, manganese, nickel, lead and zinc, and 5.3 grams of barium chromate. The ecosystem contained bacteria, Euglena, approximately 300 Tubifex (annelid worms), a few Hornwart plants, and 100 fathead minnows that were added after one month was allowed for the establishment of the rest of the system. The fish were observed to be quite healthy for a period of eight weeks. Samples of fish were removed from the aquarium at 4 weeks after their addition and at 8 weeks when the experiment was concluded. Results of heavy metal analyses on these fish are shown in Table 10.

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*Mary Sears, Ed. Oceanography AAAS, Washington, D.C., 1961, Publ. No. 67, p. 555.

Fairbridge, R.W., Encyclopedia of Geochemistry, Van Nostrand Reinhold Co., New York, p. 51.

The analytical results strongly suggest a continuing concentration of the heavy metals in the tissue of the minnows, particularly in the case of manganese and lead. In the light of the absence of adequate controls, such as analyses of minnows aging in an environment not similarly enriched, the results of this preliminary experiment cannot be considered definitive, but further study in this area is clearly desirable.

The treatment methods considered for heavy metal spills have been studied in an extensive series of experiments including beaker and channel experiments in the laboratory, and ambitious field tests. Beaker experiments in the laboratory provided verification of the fundamental chemical process involved in sulfide precipitation of heavy metals.

In an early treatment experiment, one tenth molar solutions of $CdCl_2$, $MnSO_4$, $CuSO_4$, $FeCl_3$, $ZnCl_2$, $CoCl_2$, $Pb(C_2H_3O_2)_2$, $AgNO_3$, and $HgCl_2$ were treated in 100 ml quantities with two tenth molar sodium sulfide solution. No deliberate excess sulfide was added, and the sulfide additions were measured using a 100 ml beaker with 10 ml graduations in accord with the rough control likely to be achieved in the field. Final sulfide concentration was determined using a specific ion electrode, and pH was measured with a wide range pH indicator paper. Residual metal concentrations were determined by atomic absorption spectrophotometry. Results are shown in Table 11.

Further experiments were conducted to explore the effects of pH on sulfide precipitation effectiveness. Lead acetate was used as the test material in these experiments, and varying amounts of 0.1 M sodium hydroxide solution were added to the sodium sulfide treatment. Results are shown in Figure 14. It is seen that at high sodium hydroxide additions, precipitation of lead hydroxide becomes significant and less than the stoichiometric sulfide treatment is required. Such additions present a real hazard to aquatic biota as large pH changes may be readily induced. The addition of a small amount of sodium hydroxide to the sodium sulfide solution, however, may be seen to enhance treatment before use and prevents the evolution of hydrogen sulfide gas. A solution containing 1 M sodium sulfide and 0.1 M sodium hydroxide was found to be quite effective. (This solution was not used in the experiment illustrated in Figure 14).

A series of experiments conducted in a stream simulation test facility developed for this program provided information on the transport of spills

Table 10

HEAVY METAL ANALYSIS OF FISH FROM HEAVY METAL SULFIDE EXPOSURE TESTS (ppm of wet weight)

ELEMENT	4 WEEKS' EXPOSURE	8 WEEKS' EXPOSURE
Co	1.5	1.9
Cu	3.5	4.3
Mn	14.0	21.0
Ni	3.8	3.8
Pb	17.0	21.0
Zn	47.0	51.0

Table 11

SULFIDE PRECIPITATION EXPERIMENTAL RESULTS

ORIGINAL COMPOUND	FINAL pH	FREE $S^=$ CONCENTRATION (MOLAR)	TOTAL $S^=$ CONC. (MOLAR)	RES. METAL CONC. (ppm)
$CdCl_2$	7	3×10^{-17}	3×10^{-11}	2
$MnSO_4$	7	3×10^{-8}	3×10^{-2}	n.d.* but very high
$CuSO_4$	4	$< 10^{-25}$	n.d.*	30
$FeCl_3$	7	1×10^{-12}	1×10^{-6}	200
$ZnCl_2$	12	1×10^{-4}	1×10^{-3}	2
$CoCl_2$	7	1×10^{-19}	1×10^{-13}	200
$Pb(C_2H_3O_2)_2$	n.d.*	1×10^{-20}	n.d.*	100
$AgNO_3$	8	3×10^{-7}	1×10^{-2}	0
$HgCl_2$	9	1×10^{-13}	5×10^{-10}	0

n.d.: Not Determined Exactly

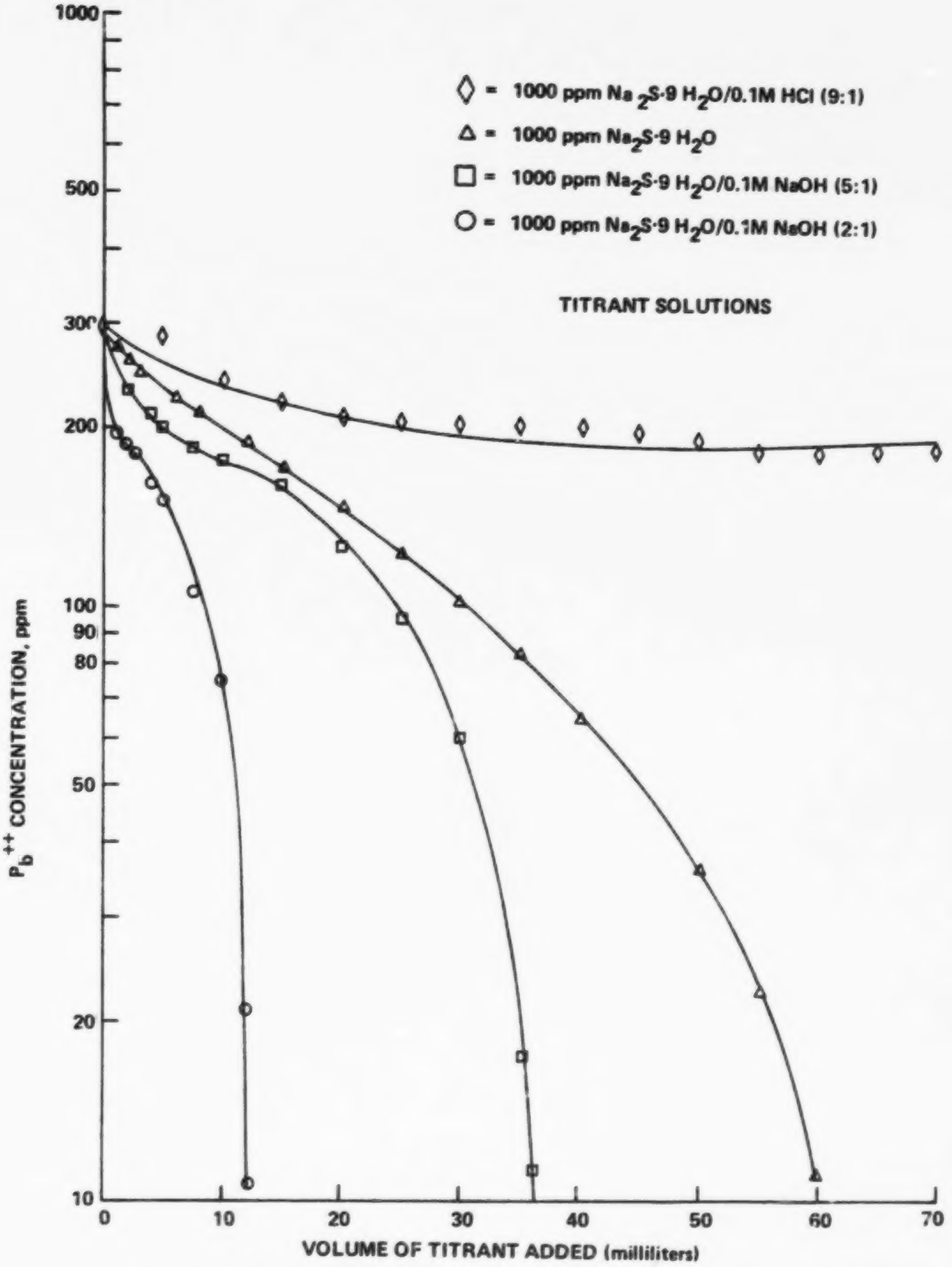

Figure 14 LEAD CONCENTRATION AS A FUNCTION OF TITRANT ADDED

and treatment under various flow conditions, and allowed evaluation of treatment methods. The effectiveness of sulfide precipitation with even the very simplest techniques for locating a spill and delivering the treatment was demonstrated.

Results of these channel tests indicated that under conditions typical of most natural streams, addition of the appropriate amount of sodium sulfide solution close to the plume of spilled material will still result in the removal of the metal from solution. Mixing in these highly turbulent flows rapidly eliminates any errors in the distribution of the treatment. Under these conditions, spill location using small quantities of sodium sulfide as a tracer is highly effective.

Under conditions of little or no flow encountered in ponds and lakes, sodium sulfide delivered off target will not mix with the metal for a long period of time. Accurate location of the spill, and proper distribution of the treatment will then be important. Introduction of some artificial turbulences (by outboard motor boats, for example) should enhance treatment effectiveness. Experiments showed that under these quiescent conditions, concentrated heavy metal solutions collected at the bottom of the water body. Measurements of ion concentration must then be made on the bottom waters of the lake or pond to be treated in order to allow proper sodium sulfide additions to be determined. Automatic spill treatment procedures as discussed earlier (Figure 11) may be useful in treating spills under these conditions. Some bodies of water such as canals and some rivers will have conditions between the extremes discussed above, and may or may not require precise treatment delivery and auxiliary mixing.

Field tests were conducted in a mountain brook using ferrous sulfate as a harmless simulant of hazardous heavy metal spills. Sodium sulfide was found to be highly effective for spill location and marking under these conditions. Rapid and thorough spill treatment was achieved by dumping sodium sulfide solution out of plastic bottles into the region which the sodium sulfide indicator solution showed to contain heavy metal ions.

Sulfide precipitation of spills of heavy metal compounds appears to be quite effective and ready for application in the field. Spills of heavy metal compounds are often small as shown in the spill statistics of Table 12 covering 1971 and early 1972.* They should be treated quickly, before the spill is diluted to a concentration less than the solubility of the metal sulfide. Thus it is important that treatment material and personnel trained in its use are available near the spill.

The recommended treatment material is a solution of sodium sulfide in water. The solution should be fairly concentrated to conserve space and reduce weight. On the other hand, crystallization of sodium sulfide at low

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*Private communication with Hal Bernard, EPA.

Table 12

HEAVY METAL SPILLS

MATERIAL	CONTAINER	CAUSE	QTY. SPILLED	SPILLED INTO
CHROMIC ACID	STORAGE TANK	RUPTURE	140 lbs	CREEK, TENN. RIVER
CHROMIUM IN ACID	STORAGE TANK	OVERFLOW	?	MILL CREEK
MERCURY	TREATMENT PLANT	LEAK	?	DETROIT RIVER
NICKEL SOL. & GROUND LIMESTONE	PILE	AVALANCHE	?	ILLINOIS RIVER
POTASSIUM PERMANGANATE	PLANT	EQUIPMENT FAILURE	11 lbs	OHIO RIVER
TETRAETHYL LEAD	RR TANK CAR	DERAILMENT	?	LAND
ZINC SULFATE	PLANT	EQUIPMENT FAILURE	7-1/2 lbs	?

temperature is to be avoided. A solution formulated at the freezing point, containing 0.85 pounds of sodium sulfide per gallon of water, and 0.04 pounds of sodium hydroxide, meets these requirements. It can be stored indefinitely at normal temperatures in plastic containers. For manual application a two-gallon bottle was found to be comfortable to carry and pour from. Rugged bottles with a molded handle, either cylindrical or in the shape of a Jerry, can be obtained for about three dollars in lots of ten thousand. As shown earlier, two gallons of treatment are sufficient for spills of two to ten pounds of common heavy metal compounds. Five gallon bottles which could treat larger spills were found to be difficult to manage in a small boat typical to a spill response situation.

Since a quick response to the spill is important, treatment should be applied by personnel near the scene. In the course of this study it was determined that firemen were interested in the spill problem and motivated to learn spill detection and treatment techniques. A police agency was interviewed and indicated that their first reaction to a hazardous spill would be to protect the public from the hazard and to ask a fire department to assist with its disposal. The agency felt that its personnel were rotated too often to benefit from spill training. These observations support the view that firemen can be trained in treating small spills. Many volunteer and paid fire companies participate in weekly training sessions that include training films on new or difficult techniques. A training film could be prepared to illustrate detection of heavy metal spills and their treatment with sodium sulfide. There are tens of thousands of fire departments in the USA. It is estimated that about ten thousand of these in conjunction with the US Coast Guard and environmental agencies of the separate states would be sufficient to cover the waterways in which a small heavy metal spill may occur. The cost of equipping all of these with sodium sulfide solution (four gallons at $0.2 each or $2000) and containers (2.80 each or $56,000), and producing and circulating training films (estimated $30,000) is estimated to be less than $100,000.

In the immediate future it would be desirable to conduct a pilot program involving the fire department(s) of an industrial city responding to real spills that might occur, and a few simulated (iron) spills in order to perfect training techniques and evaluate practical hazards of sulfide precipitation. It is anticipated that the training and administrative cost of the program will be greater than the costs of materials.

SECTION 9

IMMOBILIZATION OF HAZARDOUS CHEMICALS

The extent of environmental damage produced by any spill is dependent on the nature and quantity of spilled material and the distribution of the spill within the environment. Obvious advantages can accrue whenever it is possible to minimize the areal or volumetric extent of hazardous concentrations of spilled material either by interrupting the spill before containers are empty or by preventing the spread of material that has already spilled on land to a nearby waterway. A significant fraction of this project was devoted to these ends, and a wide variety of problems was considered.

Ideally, a spill should be terminated as soon as possible by sealing leaking or split containers before they are empty. When hazardous chemicals do spill onto the ground, immobilization of the chemical to prevent flow of hazardous liquids to surface water and to minimize percolation of liquids to subterranian aquifers should be the next line of defense. If spilled material reaches a watercourse, it is desirable to minimize the spread of floating liquids across the surface or trap water immiscible liquids in streams and ditches without interrupting the flow of water. In all of the above cases, additional advantages result if the immobilization procedure leaves the spilled material in a form which can be safely and quickly removed and packaged for further treatment, shipment or disposal.

The following methods were employed experimentally to accomplish these goals:

(1) Four powdered polymers, each capable of congealing one class of hazardous liquid into a viscous, sticky mass, were selected and combined into what has been termed colloquially "the universal gelling agent," and used to seal narrow splits in containers, to completely immobilize liquids on land, to prevent percolation into the soil, to reduce surface spreading and improve the effectiveness of booms on water, and to facilitate the trapping of liquids floating on streams in small mesh nets or screens. The resulting gel was easily removed in convenient form for subsequent treatment or disposal.

(2) Fly ash was used to absorb and immobilize hazardous liquids. When used to immobilize concentrated acids or bases, the fly ash served an additional function by minimizing the spattering when neutralizing agents were applied. Neutralization reaction rates were then determined by the amount of mechanical or hydraulic mixing applied as part of the treatment procedure. By controlling the spattering, the treatment method was made safer to use and therefore more likely to be used.

(3) Sumps to trap dense, immiscible liquids beneath flowing water and subsequent pumping to remove the spilled material from the stream were demonstrated.

(4) Sodium sulfide solutions were used to precipitate spills of heavy metal salts that had percolated into the surface. Such precipitates were found to be immobile except in association with erosion.

Results of our investigations of methods for immobilizing hazardous chemicals are summarized in the following subsections.

1. "UNIVERSAL" GELLING AGENT FOR HAZARDOUS LIQUID SPILLS. One major subclass of chemicals transported in huge volumes includes those precursor organic chemicals which by polymerization, thickening, or other chemical techniques are turned into solid end products, such as organic monomers which react to form the polymers which are the common plastics of everyday commerce. An obvious immobilization technique for this class of chemicals was to polymerize them in place at the site of the spill either on the ground or in the leaking tank. Most polymerization reactions, however, are exothermic, giving off substantial heat as they proceed so that explosion dangers are inherent in the solidification of material by this type of uncontrolled self-polymerization. In addition, a further environmental danger would have derived from the use of polymerization catalysts of the common type such as benzoyl peroxide or laurdyl peroxide, since the catalysts, themselves, are often poisonous and explosive. More innocuous thickening, solidifying or immobilizing techniques were desired. Over the course of the project, such a countermeasure was developed to encompass a wide variety of hazardous spills, including monomers, organic solvents, feed stock chemicals, and inorganic reactants.

The mechanism by which the "universal gelling agent" acts is as follows. The individual gel components selectively interact with the appropriate chemicals themselves to create an immobile semi-solid mass which is easily removed by mechanical means. This is in contrast to other spill immobilization techniques which have been described and demonstrated, which simply absorb the spilled liquid into a finely powdered mass of inexpensive, easily accessible, easily deployable materials (such as fly ash or Portland cement) with few, if any, secondary environmental hazards.

The "universal gelling agent" represents a new formulation created by the mechanical blending of at least four and preferably five or more specific ingredients, each having a specific purpose. The first ingredient is a material of the highly water-soluble polyelectrolyte-type, typified by polyacrylamide. This material could be substituted by any of a number of other polymers including proteinaceous materials such as gelatin and casein. It is important that this powder, and all the other components of the blend, be particle-size controlled within a precise range for speedy interaction with the target liquid, and for ease of deployment. It should also be manufactured or admixed with a small surface-active additive to assure rapid contact with aqueous liquids.

The second component of the blend is a loosely cross-linked copolymer of the ilk typified by polytertiary-butystyrene copolymerized with divinylbenzene. This material is selected to ineract most strongly with those liquids having low polarity (such as cyclohexane, gasoline fractions, and a variety of other inert spirits).

A third component is a material of the polyacrylonitrile-butadience copolymer class which is chosen to be especially effective against polar organic chemicals such as acrylonitrile, ethylene dichloride, and other chlorinated liquids.

The fourth component of the gelling agent is a material to cope with the most difficult of all hazardous liquids to thicken, solidify, and immobilize in place, as typified by methyl alcohol and other chemicals of the alcoholic class. Materials suitable for this use include the polycarboxylmethylcellulose polymers or the polyethylene oxide materials. For these types of polymers, one of the less expensive polysaccharide exudates produced by bacterial cultures can be substituted.

The four component blend used experimentally on this program consisted of equal parts of:

(1) Dow Chemical Corporation, Gelgard, to combat spills of aqueous liquids,

(2) Dow Chemical Corporation, Imbiber Beads, for spills of the inert spirits-type liquids (typified by cyclohexane),

(3) BF Goodrich Corporation, Hycar 1422, to combat the polar organic chemical spills including the chlorinated hydrocarbons, and

(4) BF Goodrich Corporation, Carbopol (and in some cases, Union Carbide, Polyox) to selectively thicken and control alcohol spills.

Ease of delivery of this four-polymer blend required fluidization to ensure rapid, smooth egress from commercial spray equipment. A one-fifth by proportion addition of fumed silica "Cabosil," produced by Cabot Corporation was used. It is well-known in the paint and pigment industry that such finely powdered silicas can be used as thickeners for most organic vehicles. While the kinetics of such thickening action are far too slow to be useful in the manner envisaged here, the addition of Cabosil to the "universal gelling agent" for the primary purpose of fluidizing the blend for ease of field deployment had the secondary benefit of providing a stiffer, hydrolysis-resistant gel of almost all hazardous liquids tested.

Consultation with manufacturers of the polymers mentioned in the preceding paragraphs and with others in competitive industries indicated that the final cost for the "universal gelling agent" can be brought to 50¢ per pound or less. The chemicals against which the "universal gelling agent" has so far been tested, with excellent results, are listed in Table 13. It was learned from laboratory experiments that approximately 10 to 25% of the "universal gelling agent" by

Table 13

COMPOUNDS TESTED WITH UNIVERSAL GELLING AGENT

- ACETONE
- ACETONE CYANOHYDRIN
- ACRYLONITRILE
- AMMONIUM HYDROXIDE
- ANILINE
- BENZALDEHYDE
- BENZENE
- BUTANOL
- CARBON DISULFIDE
- CARBON TETRACHLORIDE
- CHLORINE WATER (SATURATED)
- CHLOROFORM
- CYCLOHEXANE
- CYCLOHEXANONE
- ETHANOL
- ETHYLACETATE
- ETHYLENE DICHLORIDE
- ETHYLENE GLYCOL
- FORMALDEHYDE
- GASOLINE
- ISOPRENE
- ISOPROPYL ALCOHOL
- KEROSENE
- METHANOL
- METHYL ETHYL KETONE
- OCTANE (2,2,4 TRIMETHYL PENTANE)
- ORTHO-DICHLOROBENZENE
- PETROLEUM ETHER
- PHENOL (89%)
- PYRIDINE
- SULFURIC ACID
- TETRAHYDROFURAN
- TRICHLOROETHYLENE
- WATER
- XYLENE

weight, based upon the weight of the original spilled liquid, is required for complete immobilization. Field studies have shown, on the other hand, that it is usually necessary--because of inefficiencies inherent in field deployment of the material and the poor mixing usually obtained--that a minimum of double this theoretical amount is regularly required.

The results obtained with the experimental blend used on this program demonstrate the potential value of the gelling agent for combating liquid spills. Little effort was devoted on the program to optimizing the blend either from the utilitarian or cost-effectiveness viewpoints. It is recommended that additional effort be devoted to optimization of the agent in preparation for operational use.

2. FIELD EXPERIMENTS. Most of the field experiments performed on the project were designed to investigate methods for immobilizing hazardous chemicals. These experiments were performed at a half square mile tract of abandoned farmland owned by Calspan near Bethany, New York. After a series of soil tests showed that the possibility of significant percolation of purposely-spilled chemicals into subterranean aquifers or surface drainage into nearby streams was negligible, the experimental facilities depicted schematically in Figure 15 were constructed.

Two sets of ditches, 2 feet wide by 2 feet deep and 100 feet long, were constructed with 1% and 2% grades, respectively, to determine the effectiveness of immobilization procedures against surface flow of spilled materials. At the foot of each set of ditches, a large excavation was constructed to house two, 12-foot diameter, 3-foot deep, plastic-lined swimming pools intended to capture all spilled material before escaping to the natural environment. The basic experimental concept used in most experiments was to simulate two spills in each experiment. One spill was treated experimentally in an effort to immobilize the chemical and a second was used as a control: i.e., to establish a baseline against which the behavior of the treated spill could be compared.

In accordance with the general theme of this project, the chemicals used for experimental spills in the field were selected to represent classes of materials that pose serious hazards in the real world. Pure water was used to simulate weak aqueous solutions. Cyclohexane was selected as a serious real threat which is representative of chemicals which are immiscible with water and float on the surface, while ethylene dichloride was selected to represent immiscible chemicals that are more dense than water.

Sulfuric acid, the hazardous chemical shipped (through the United States) in greatest quantity, was chosen in an attempt to solve the special problem of frothing that has produced serious equipment damage during treatment of land spills of acids and bases with neutralizing agents. In attempts to immobilize heavy metals, the eventual fate of the compound used in the experiments could not be predicted. Therefore, a relatively harmless compound, manganese sulfate, was selected for experimental use. The results of these experiments are summarized below.

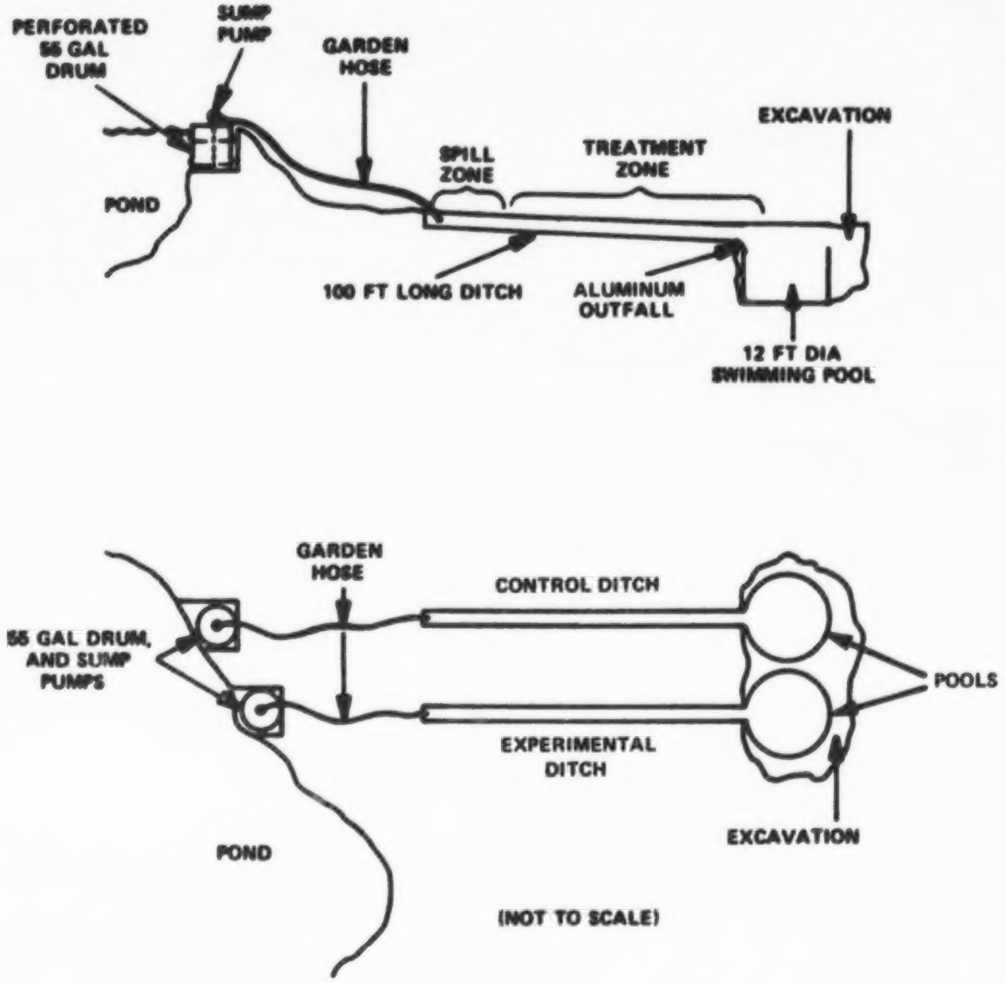

PERFORATED 55 GAL DRUM
SUMP PUMP
GARDEN HOSE
POND
SPILL ZONE
TREATMENT ZONE
EXCAVATION
100 FT LONG DITCH
ALUMINUM OUTFALL
12 FT DIA SWIMMING POOL
GARDEN HOSE
CONTROL DITCH
55 GAL DRUM, AND SUMP PUMPS
POOLS
EXPERIMENTAL DITCH
POND
EXCAVATION
(NOT TO SCALE)

Figure 15 EXPERIMENTAL FACILITY AT BETHANY TEST SITE

3. IMMOBILIZATION OF LAND SPILLS WITH GELLING AGENTS. To minimize cost and clean-up problems after experiments, specific gelling components were used in all large-scale field experiments. The "universal" agent was tested only in the laboratory.

Initial immobilization experiments in the field were performed with pure water spills to represent weak aqueous solutions and to develop safe and effective field test treatment procedures before using hazardous chemicals. In these experiments, Gelgard was used exclusively as the gelling agent. Ten such experiments were performed on 55-gallon water spills in the 1% and 2% ditches.

The manufacturer recommends 0.4% by weight (1.8 lb/55 gallons) of Gelgard to congeal water. In the field tests, dosages ranging from 2 to 6 pounds were used to immobilize one to five-minute long 55-gallon spills in distances ranging from 25 to 75 feet in the ditches. The overtreatment was required to compensate for inefficient distribution of the agent on the spill. The poor distribution was caused mainly by the powder's falling on already congealed water and by the need to create a stiff gel to break the momentum of water at the head of the flow, creating a dam capable of retaining the pressure of as-yet-untreated water. Since ditches were always saturated with water before experiments, the control spills of water always resulted in 55 gallons flowing over the outfall 100 feet downstream.

To minimize the area affected by the spill, it is necessary to inhibit flow as soon as possible. It is therefore particularly important to treat the head of the flow first. Not only does this create a dam to interrupt the flow, but the head is a region of turbulence which produces excellent mixing of the agent with the liquid, promoting efficient treatment. Typically, the first dam of congealed material reached a depth of 1/2 to 1 inch before overflow began. It was most effective then to move downslope to form a second dam. With the flow inhibited by the first gel dam, the second was more easily formed, and by continued treatment was built to depths sometimes exceeding 2 inches before overflow began. By progressive treatment in this way the final dam usually exceeded four inches in depth with a 55-gallon spill before flow was terminated in the ditch. Once this was accomplished, it was a simple matter to move upstream and treat the liquid trapped behind the dams that had been formed earlier.

Several dispersal methods were tested with Gelgard in these experiments. It was apparent that broadcasting the agent with shovels was a simple and effective procedure for spills with minimum dimension of four to five feet. Much of the material was lost in our narrow ditches with this procedure. When attempts were made to sprinkle the material from shovels, the distribution of the agent across the surface was usually uneven. As water flowed around the thicker regions, an impenetrable gel formed at the surface, producing a large clump with dry, unused agent at its center. For more uniform distribution, sprinklers resembling salt shakers were constructed from three-pound coffee cans to which six-foot long handles were attached. These sprinklers proved to be very effective for treating in narrow confinements and were used extensively in subsequent experiments.

Hand pump dusters normally used for insecticide application in home gardens could not deliver the agent fast enough to stop a 1/2-gallon per second flow in the 2-foot wide ditches. Larger hand-powered dusters intended for agricultural use delivered material at an adequate rate but were so tiring that continuous operation could not be maintained. This type of duster could be equipped with battery-powered explosion-proof motors to produce effective portable equipment for treatment of spills that have reached remote areas (e.g., where the spilled material flows into heavily wooded areas through gulleys or small streams).

Dry chemical fire extinguishers produced an airborne plume of agent that was too wide to treat spills in confined areas. Since fire extinguishers cannot hold a sufficient mass of agent for treating large spills, they do not seem practical for use against material that is already on the ground. However, with a modified nozzle design, they could be made into very effective portable devices for sealing narrow splits in containers.

High pressure dispersal devices appear to be suitable for immobilizing large spills that require large amounts of gelling agent where the use of compressor-operated equipment is appropriate. Although paint sprayers proved effective, they could not deliver the agent at a sufficient rate to treat large spills. In these experiments, sand blasters, deliverying 5 to 10 pounds of agent per minute, provided an appropriate distribution for large spills even though some of the agent was always blown out of the simulated spill area by the wind.

The bulk of gelled material was easily removed mechanically by shoveling th[illegible]erial into 55-gallon drums. Heavy earth-moving equipment could be usef[illegible] large spills of nonflammable materials, but should be avoided where a f[illegible]zard exists. The sticky consistency of most gelled chemicals makes pum[illegible]g inappropriate at least for land spills.

Typically, 75 to 85% of the spilled material was recovered in gelled form during our experiments. Our experience was that some material was always inaccessible to shovels after gelling chemicals on land. But the amount was a small fraction of the mass lost in control experiments by a combination of evaporation and percolation into the soil when the ditches had not been presaturated with water before the experiment. In some cases in which Gelgard is used on highways or city streets, thorough washdown should be required to eliminate the lubricating effect of dilute mixtures of this material and water. Like most polyelectrolytes, Gelgard produces a nearly friction-free environment that could be extremely hazardous to pedestrian and automotive traffic. Manual scrubbing followed by thorough rinsing would be adequate for small spills. Vacuum scrubbers commonly used on airports for hangar floor and ramp washing would be ideal for clean-up after treatment of large spills. Before leaving the area of a spill treated with Gelgard, all affected surfaces should be tested while wet, since friction is not affected by the dry form.

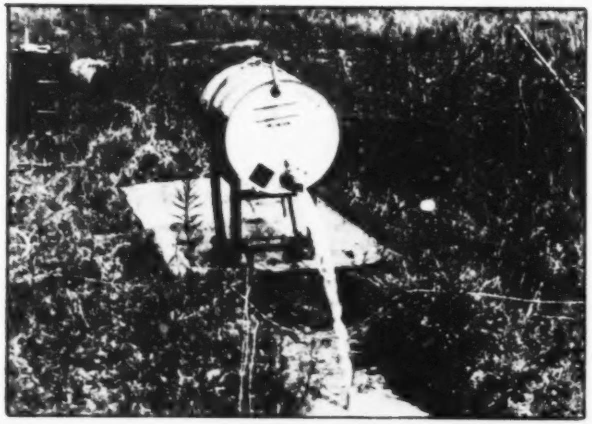
In addition to the experiments with water, experiments were performed in the ditches to test immobilization procedures against cyclohexane and ethylene dichloride. In both cases, the 2% ditches were saturated with water but no standing water was present. Seventy-five pounds of Imbiber beads were used to completely immobilize the 55-gallon cyclohexane spill within 80 feet of the spill point. Forty-one and one-half pounds of Hycar arrested the 55-gallons of ethylene dichloride in slightly less than 70 feet. After the treatment was completed in each case, water was pumped through four garden hoses into the spill zone to determine if the gelled material could be dislodged. As water seeped under the cyclohexane, buoyancy dislodged approximately 50% of the material in 30 minutes, but none flowed down the ditch. The ethylene dichloride was unaffected. A surge flow of water, produced by releasing 55 gallons at the head of the ditch in 2 minutes, washed approximately 75% of the gelled cyclohexane into the pool. The consistency of the floating material was such that it could easily have been trapped with a small mesh net or screen. Again, the ethylene dichloride was unaffected. In both cases, a total of 75% of the spilled material was recovered in gelled form by shoveling and 75% of the respective control spills was flowed into drums placed at the outfall 100 feet downstream. A sequence of four photographs are included in Figure 16 to illustrate the results of these experiments.

Thus, it was demonstrated that significant benefit can be achieved by using gelling agents to immobilize land spills of these two classes of materials.

4. PROTECTION OF PERSONNEL AND PROPERTY. The experience acquired in preparing for and executing these experiments constituted an extremely valuable portion of the overall results. Since the chemicals used in these demonstrations were toxic by skin contact and inhalation, and represented significant fire hazards, a variety of safety precautions had to be followed. Similar and improved preparations must be made in advance for the protection of members of clean-up teams for real spills.

Gas masks and air packs were provided to team members working in areas of potential hazards from vapors of the spilled material. Oxygen was available in case of inadvertent inhalation of vapors in spite of these precautions. In addition, two vapor sensors were used to warn against potential hazards either from inhalation or fire.

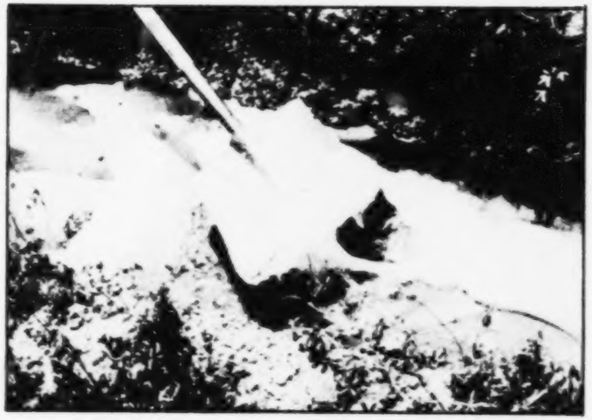
Protective clothing, including boots, trousers with elastic ankle bands, slip-over jacket with hood and elastic waistbands, and gloves, were provided to all workers. When worn with face masks, the clothing seemed quite adequate as temporary protection against skin contact. Garden hoses with running water were available continuously to rinse these garments in case of minor splashing or immersion. A small plastic swimming pool filled with water was maintained on site for total immersion of any team member suffering extensive contact with the spilled chemical.



(A) TYPICAL SPILL CONFIGURATION

(B) TREATMENT WITH GELLING AGENT

(C) COMPLETE IMMOBILIZATION
IN 79 FEET IN THIS CASE



(D) REMOVAL OF GELLED MATERIAL WITH ALUMINUM SHOVEL. MAXIMUM THICKNESS OF CONGEALED CYCLOHEXANE WAS ABOUT 4 INCHES IN THIS EXPERIMENT

Figure 16 IMMOBILIZATION OF HAZARDOUS CHEMICALS ON LAND WITH GELLING AGENTS

Two types of protective suits* were used in these experiments. Disposable plastic garments available from Protective Clothing Supply** were light and fairly comfortable but were more susceptible to tears and abrasions than the heavier reusable garments available. Both types of protective gear were extremely warm when worn in sunshine and neither type offered significant protection against fire.

Significant improvements could be made in protective clothing. For example, incorporating a metallized finish with the fabric or plastic would seem appropriate to reflect heat from the sun for increased comfort and, more importantly, to offer some protection against the initial flash and subsequent radiation from fires.

With the materials used in our experiments (and many of the spills that occur in the real world), the fire hazard is by far the most serious. We protected ourselves at the Bethany site by limiting experiments to conditions with minimum windspeed of 5 mph, carefully monitoring the vapor concentration in the working area and simply leaving the area once when the vapor concentration in the ditch exceeded the lower explosion limit. Our plan for fire was to let it burn and use fire extinguishers only to assist in rescue operations if necessary. Such behavior is not acceptable in the real world where the spill site cannot be selected and carefully prepared with fire breaks in advance. The potential fire hazards must be considered in each spill and suitable tactical measures must be implemented for protection of personnel and property. Additional research is required to develop countermeasures which are specifically applicable to the spill situation.

Only two concepts for minimizing the fire hazard were test on this program. Attempts were made to mix a variety of dry chemical fire-fighting agent with the universal gelling agent in the hope that if a fire started, the CO_2 generated by combustion of the gel would extinguish the fire or at least reduce its intensity. But laboratory experiments showed that even with 50% dry chemical fire-fighting agents, there was no significant reduction of hazard. Dry chemicals and foam were effective, however, for extinguishing fires fueled by the gelled material.

The second approach, that of reducing evaporation of spilled material to maintain incombustible vapor-air mixtures above the spill, was more successful. To accomplish this end, the spilled material was treated with a high density fire-fighting foam before application of the gelling agent. These vapor suppression experiments were performed on a specially-equipped test pad used for a variety of fire-fighting experiments at Calspan. The test pad (Figure 17) consists of a concrete floor with three concentric steel rings which are held in the concrete and rise 3 inches above the concrete surface. The liquid level within the concentric rings is equalized

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[*] "Safety First" Disposable two-piece suits with hood.

[**] 1243 Military Road, Buffalo, New York.

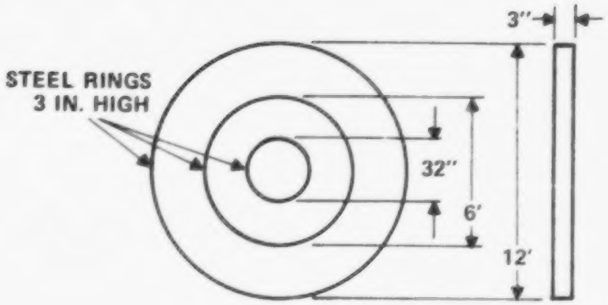

STEEL RINGS
3 IN. HIGH
3"
32"
6'
12'

Figure 17 SKETCH OF PAD FOR VAPOR SUPPRESSION TESTS

Table 14

LIST OF FOAM CONCENTRATES FOR FLAMMABLE LIQUID

NATIONAL'S FOAM LIQUID	FLAMMABLE LIQUID
AER-O-FOAM XL-3	ETHYLENE DICHLORIDE CYCLOHEXANE
AER-O-FOAM "99"-6%	METHANOL

through holes in the rings. Fifty-five gallons of flammable liquid on the test pad forms a pool approximately 1-1/2 inches deep.

Two instruments were used to measure the reduction in vapor concentration above the spills: a Johnson-Williams Model CD 800 W with recorder output, and a model G vapor sniffer. These instruments measure the percent by volume of the vapor in air and give a meter reading calibrated in the percent lower explosion limit (%LEL) for the vapor. An explosion could occur at 100% LEL. The devices used were calibrated for methanol, which has the lowest LEL of materials used in the experiments. Vapor measurements were made at known distances from the liquid surface of the spill before and after application of the foam.

High density foam was applied with a National Foam System, Inc. "Hand-held Nozzle" Model RP-6B with the HL metering-check valve combination connected directly to the nozzle. Table 14 lists the foams and the flammable liquids on which they were used.

The foam was applied by splashing it in front of the outside steel ring so that it would gently flow onto the flammable liquid. Approximately 2.5 gallons of foam concentrate were applied in each of the 3 experiments which took approximately 50 seconds each time. The resultant foam depths over the flammable liquids ranged from 1/2 to 1 inch.

The results of these experiments are summarized in Table 15 . Note that in each case, the vapor concentration was reduced by a factor of at least three. Best results, reduction by factors of 6 to 10, were achieved with the cyclohexane and ethylene dichloride which are water insoluble. It was postulated that as the foam rolled onto the methanol, some of the methanol was dissolved by the water in the foam and transported to the top of the foam layer.

All the experiments were performed in fresh-to-moderate breezes, which limited the initial vapor concentration (measured 1 to 3 inches above the surface of the spill) to low values. Significantly better improvement ratios were observed under the quiescent conditions of the laboratory, where high initial concentrations existed at the same distance above the surface.

In each of these three experiments, specific gelling agents were used: Imbiber beads for cyclohexane, Hycar for ethylene dichloride, and Carbopol for methyl alcohol. In all cases, the presence of the foam appeared to inhibit contact between the spilled liquid and the powdered treatment. Vigorous mixing was required to promote gelling.

In subsequent experiments performed on a laboratory scale, each of the specific gelling ingredients was mixed with Gelgard and applied to foam-treated surfaces of the same flammable test chemicals. In each case, the Gelgard reacted with the water in the foam and caused it to disperse. The remaining ingredients apparently remained free to react with the flammable liquids since gelling of these materials proceeded at a more nearly normal

Table 15

SUMMARY OF RESULTS ON COMBINED
VAPOR SUPPRESSION AND GELLING TESTS

FLAMMABLE LIQUID	VAPOR READING IN L.E.L. (%)		GELLING MATERIAL AND AMOUNT (lb.)	COMMENTS
	NO FOAM	WITH FOAM		
ETHYLENE DICHLORIDE	6–8	0.8	HYCAR 1422 60	FOAM APPEARS TO SLOW GELLING ACTION. MAY BE DUE TO BOTH FLUOROCARBON AND WATER USED TO GENERATE FOAM.
CYCLOHEXANE	24	4	IMBIBER BEADS 55	LARGE BEADS WERE USED; THESE REACT SLOWLY. HERE AGAIN INTERFERENCE WITH FLUOROCARBON AND WATER IS SUSPECTED.
METHANOL	6	2	CARBOPOL 50	CARBOPOL SEALS ITSELF OFF WHEN APPLIED BY HAND LEAVING UNREACTED MATERIAL INSIDE LARGE CLUMPS; REQUIRED MIXING TO GET GELLED PRODUCT.

rate. But the effectiveness of the foam in minimizing the fire hazard was substantially reduced.

These experiments suggest that in a large spill the fire hazard due to spilled liquids might first be minimized by coating the entire spill with foam. The universal gelling agent might then be used to treat relatively small portions of the spill-affected area. When gelling is complete in one area, additional foam could be applied while the gelling treatment is applied elsewhere. By such a procedure, the overall fire hazard might be kept to manageable proportions. Before firm conclusions can be drawn, however, testing would be required.

In addition, only high-density foams were tested on the program. Considering the variety of fire-fighting foams and application techniques available, substantially more testing is warranted before making specific recommendations.

5. THE USE OF GELLING AGENTS ON WATER SPILLS. Limited small-scale experiments using gelling agents to immobilize hazardous liquids floating on water showed that the fraction of liquid that had not gone into solution could be readily congealed. In tests with benzene, cyclohexane, and gasoline, the congealed material continued to float indefinitely. Hycar-treated acrylonitrile, on the other hand, floated for approximately 48 hours in the beaker experiments and then gradually sank to the bottom. (Bioassay tests with both benzene and acrylonitrile showed that fathead minnows mistook small floating particles of gelled material for food and died within a few hours. These tests may not be valid, however, since the aquarium fish were trained to eat food sprinkled on the surface.) The ease and speed with which the gelled material could be removed from the water surface suggest, in any case, that the procedure could be quite useful and that larger scale tests are warranted.

Several large-scale laboratory experiments were performed in 12-foot diameter swimming pools to determine the effectiveness of gelling procedures for immobilizing spills of materials which are immiscible with water and less dense than water. Cyclohexane was used as the test material and Imbiber beads were used for treatment.

Cyclohexane spilled on clean water initially forms thin beads that persist for several minutes. After minor agitation, presumably as a result of a small amount of cyclohexane going into solution locally, the bead spreads spontaneously into an extremely thin film. In a variety of experiments in which cyclohexane was both spilled from beneath the water surface and poured onto the surface, the spontaneous spreading was prevented by treatment with Imbiber beads. As spillage and treatment continued, the gelled material reached thicknesses up to approximately a half centimeter as it gradually drifted outward from the spill center. Light breezes caused noticeable drift of rafts of the congealed material, and no tendencies to sink were observed.

The gelled cyclohexane could be readily confined and immobilization completed with unsophisticated booms constructed of short lengths of 4 x 4 lumber to which screen wire had been attached. These booms completely confined the gelled material and permitted it to be compressed to thicknesses of about four inches.

Field experiments were performed with this hazardous material at our Bethany site. The 15-by-30 foot excavation at the foot of the 1 percent ditches was filled with water to simulate a lake. A 24-foot boom constructed of 4 x 4's, screen, and an 8-inch plastic skirt was placed around the outfall in such a way as to confine the spilled material to about one quarter of the excavation surface. Fifty-five gallons of cyclohexane were spilled 15 feet upstream from the outfall of a ditch in which a continuous water flow was maintained with two garden hoses. The experimental configuration is shown in Figure 18 . Sixty pounds of Imbiber beads were broadcast onto the spill from shovels as the cyclohexane entered the excavation. As in the pool experiments, the treatment was highly effective. The cyclohexane was congealed into a floating mass with an average thickness of approximately 1/4 inch that was completely contained within the boom. The boom was used to corral the treated material to the ramp area of the pond (See Figure 18) and to compress the gell to thicknesses up to 2 inches without loss. Aluminum shovels were then used to skim the 1-to-2-inch layer of stacked gelled material from the water into 55-gallon drums. Approximately 75% of the original spill volume was collected from the ramp area. The losses can be attributed to evaporation and to adhesion to the walls of the excavation. These results are illustrated in the four photographs presented as Figure 19.

After removal of the bulk of the gel, the surface of the pond was swept with a piston film of Sorbitan Monooleate to complete treatment. Bulk water contained 3.8 ppm of cyclohexane.

There was no control test performed in conjunction with this experiment. There is little doubt, however, from tests performed in swimming pools that untreated cyclohexane would have escaped through the crude boom and covered the entire excavation. A skimming operation involving special equipment would have been required to recover the spilled material.

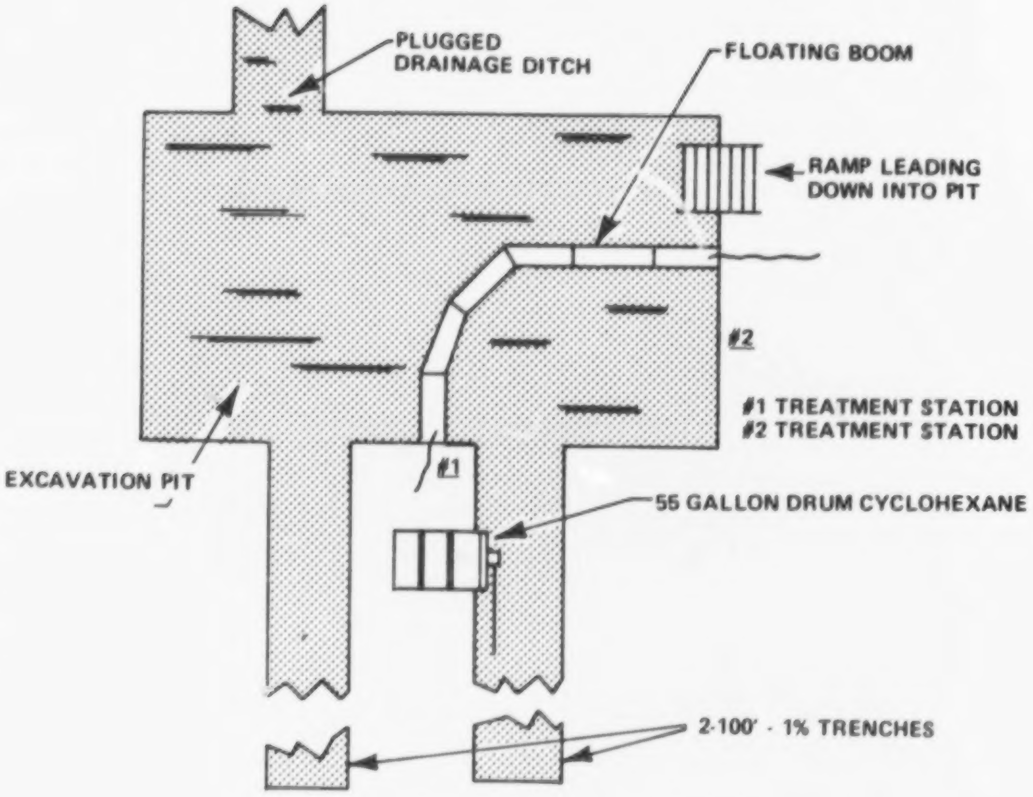
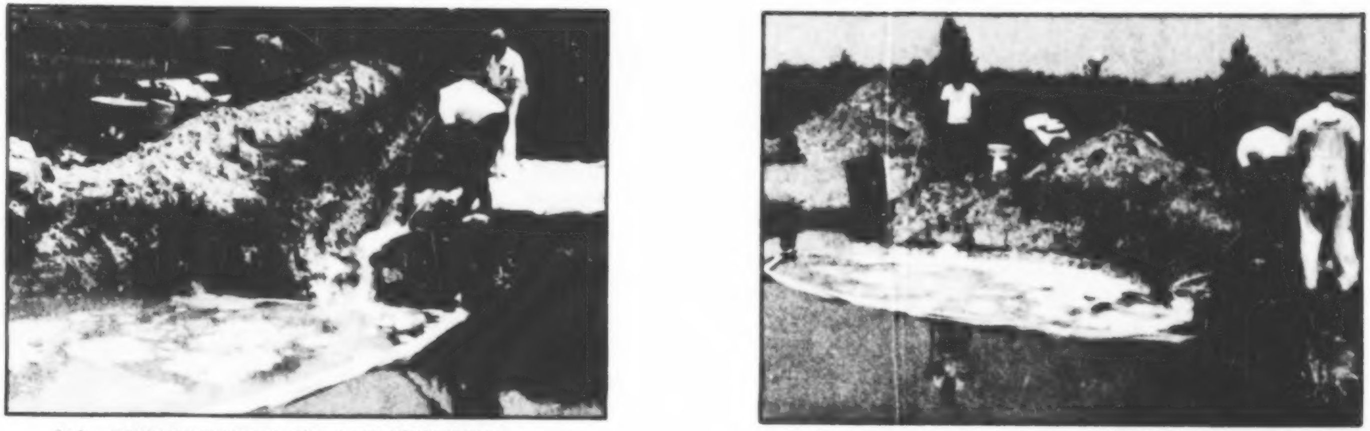
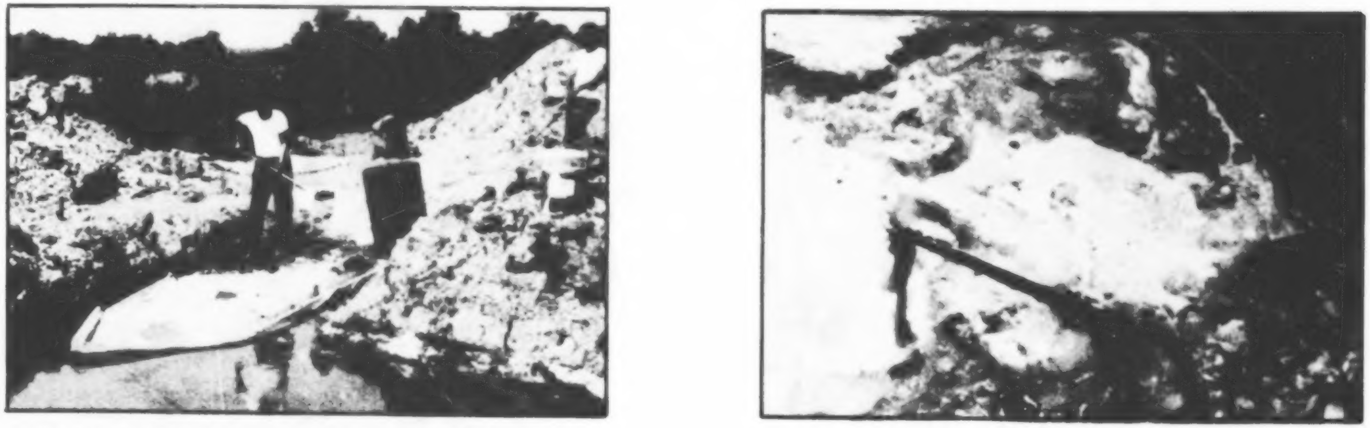

PLUGGED DRAINAGE DITCH
FLOATING BOOM
RAMP LEADING DOWN INTO PIT
#2
#1 TREATMENT STATION
#2 TREATMENT STATION
EXCAVATION PIT
#1
55 GALLON DRUM CYCLOHEXANE
2-100' - 1% TRENCHES

Figure 18 PLAN VIEW OF "LAKE" CYCLOHEXANE SPILL TREATMENT TEST



(A) CYCLOHEXANE SPILL IN PROGRESS
AND TREATMENT WITH IMBIBER BEADS

(B) THE INITIAL BOOM CONFIGURATION



(C) BOOM TOWED TO RAMP AREA FOR
REMOVAL OF GELLED CYCLOHEXANE

(D) NOTE ABOUT 2-INCH THICKNESS
OF GEL IN BOOM AND SHOVEL

Figure 19 INCREASING THE EFFECTIVENESS OF BOOMS BY CONGEALING THE TRAPPED LIQUID

6. GRAVITY COLLECTION OF HEAVIER-THAN-WATER CHEMICALS IN STREAMS. An experiment was performed to determine whether or not liquids that are immiscible with water and have a specific gravity exceeding unity could be effectively trapped in an artificial depression in a stream bed. Ethylene dichloride (specific gravity: 1.1) was used as the test material in one of the ditches with a 2% gradient. For the demonstration, an excavation was made in the trench approximately 75 feet from the spill drum.

To simulate a very slow-moving stream, a sandbag dam was constructed below the excavation and the ditch was filled with water until the dam overflowed. Water was allowed to back up into the trench to a position about 40 feet above the excavation. A 250 ml beaker was placed in a small depression between the excavation and the dam. The experimental configuration is illustrated schematically in Figure 20. The 55-gallon spill was accomplished in two minutes from the position indicated in the figure. Three hoses maintained a continuous flow (about 15 gpm) of water from the spill zone over the dam.

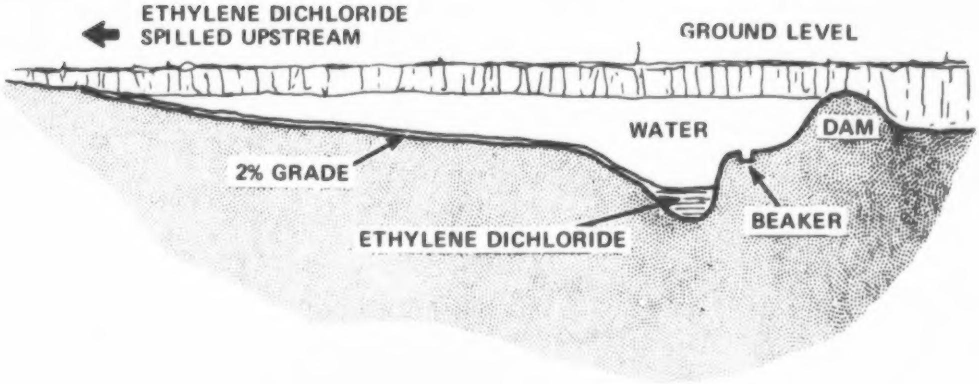


Figure 20 CROSS SECTION OF THE DITCH AS MODIFIED TO TRAP HEAVIER-THAN-WATER SPILLS

Immediately after spilling at the end of the trench, the solvent formed large streaming beads that moved with the shallow flowing water. Small pockets of the material were trapped in depressions along the bottom of the trench and in turbulent eddys behind a few large clumps of clay that had fallen into the trench. Upon reaching deeper water (approximately 1/2 inch), the material settled completely beneath the surface of the water and continued to flow under the influence of gravity into the excavation. When the spill had been completed and flow of ethylene dichloride could no longer be detected in the ditch, the beaker was removed and found to contain no visible ethylene dichloride. It was then replaced. The "sniffer" did not detect ethylene dichloride vapors above the water surface, but small concentrations were detected above trapped beads of solvent. These beads, incidentally, could be easily dislodged by agitating the water in the vicinity of the obstruction or depression.

After a variety of peripheral experiments of this kind, the dam was removed to produce rapid flow of water over the excavation and thereby simulate the effect of a fast stream. When the flow had reached equilibrium, the beaker was again removed. Several additional surge flows were produced by spilling 55 gallons of water into the ditch and additional beaker samples withdrawn. In no case was ethylene dichloride visible in the beaker.

Collected material was then pumped with a submersible pump from the depression in the trench to another drum. Forty-seven gallons were recovered.

Samples of water which overflowed the dam were analyzed for ethylene dichloride using a H/P 5750 gas chromatograph with a flame ionization detector. The samples collected from the beakers (mounted between the depression and the dam) were found to have ethylene dichloride concentrations ranging from 300 ppm before the surge flow to 4400 ppm after the surge flow, which may be compared with the nearly pure ethylene dichloride in the bottom of the depression. When the dam was removed to initiate surge flow, ethylene dichloride concentration was measured at 2000 ppm in a sample collected at the outfall. A sample of water collected from the overflow of the dam just before the surge flow was produced contained only 4.4 ppm ethylene dichloride. It is not known whether the higher concentrations that accompanied the surge flows were due to entrainment of ethylene dichloride from the excavation or due to entrainment of water that had rested above the ethylene dichloride in the excavation for long periods of time and thereby contained the solvent in solution, but in either case it is concluded that removal of sunken hazardous material should be undertaken whenever possible to minimize contamination of the water column.

Based on our small-scale field tests, the separation of substances with specific gravity exceeding one from water by gravity appears to be a viable way to recover spills in waterways. Conceivably, advance notice of an upstream spill would provide time for an excavation to be produced in a downstream location for the entrapment of the denser material traveling along the stream bottom.

Benefits of this technique include:

1. High percentage recovery of original spill volume.
2. Spill material in many cases may be recovered in nearly unadulterated, easily recoverable form.
3. Minimum investment in equipment required.
4. Materials and equipment used are easily obtained.

In consideration of the use of this technique, it must be recognized that artificial excavations must be made in streams. The natural depressions in streams are present because the hydrodynamics in the stream is such that heavier-than-water bottom sediments are naturally removed from those locations. While such locations should be searched for pockets of trapped material, it is not reasonable to expect that a given natural depression would trap significant quantities for long periods of time.

7. TREATMENT OF SULFURIC ACID LAND SPILLS. One of the principal problems that has occurred in attempting to treat concentrated acids and bases spilled on land is caused by the severe bubbling and frothing that occurs when large quantities of neutralizing agents are bulldozed into the pool of material. Particularly difficult situations have been reported when treating sulfuric acid spills with lime. In consideration of this problem, it was reasoned that a process that would permit the control of the reaction rate could be of value. One concept that evolved was the use of fly ash to absorb and immobilize the acid. The limestone could then be added after immobilization was complete. Under such conditions, neutralization would occur only at the surface of contact between the two materials. After the frothing that accompanied the initial contact had ceased, the two substances could be periodically mixed at a controlled rate by some remote means to cause the reaction to occur after equipment and personnel had been removed to safer locations.

After laboratory tests indicated that significant control could be achieved by this means, a small field demonstration was performed. A 15-gallon neoprene drum of sulfuric acid was placed in the bottom of a 100-foot, 1% grade trench, approximately 10 feet from the upstream end. One hundred pounds of fly ash was placed 10 feet downslope from the acid drum, while four piles of lime were strategically located at intervals directly downstream from the fly ash dam, as illustrated in Figure 21.

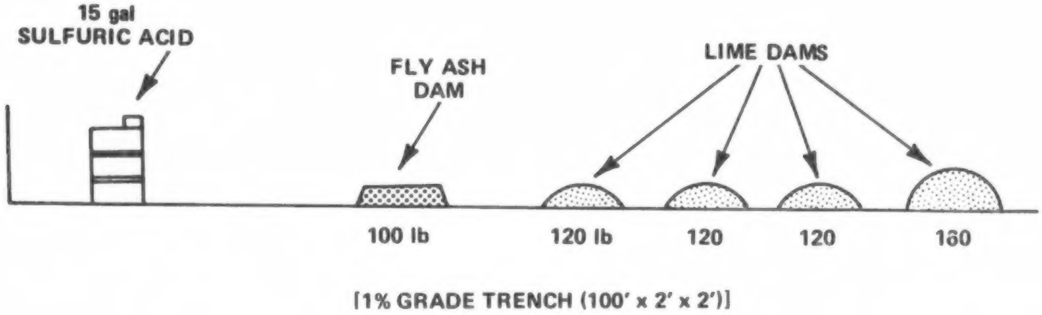


Figure 21 TREATMENT OF SULFURIC ACID SPILL

The measured pH's of pond water, water in the flooded excavation at the end of the trench, and residual water puddled in the bottom of the trench, were 8.0, 7.9, and 8.0, respectively, before spilling the acid. Three control lines were attached to the container of sulfuric acid. Personnel outfitted with complete sets of protective clothing, including PVC suits, rubber boots, neoprene gloves, and protective goggles, adjusted tension on the lines to trip the acid drum and produce a controlled spill.

The initial fly ash dam effectively prevented flow of sulfuric acid in the trench, but seepage into the fly ash was slow. In the interest of time, an additional 50 pounds of fly ash were shoveled on top of the liquid acid to form a stiff slurry, which included all of the fly ash in the initial dam. Two hundred twenty pounds of crushed limestone were then shoveled onto the slurry. There was an initial strong reaction of lime with the acid with frothing caused by CO_2 evolution ($H_2SO_4 + CaCO_3 = Ca\ SO_4 + CO_2 + H_2O$). This reaction subsided after five minutes and was reiterated upon mixing with a garden rake. Reaction rate was found to be controlled by degree of mixing.

The degree of control of the reaction rate which can be achieved by this procedure is vividly illustrated with the two photographs presented in Figure 22. The froth formed by the initial layer of lime on the acid fly ash slurry is visible in Figure 25A just above the shovel handle. The second lime layer is visible on top of this subsided froth layer in the lower right corner of the photograph. No evidence of a chemical reaction is indicated where the lime and froth layer meet.

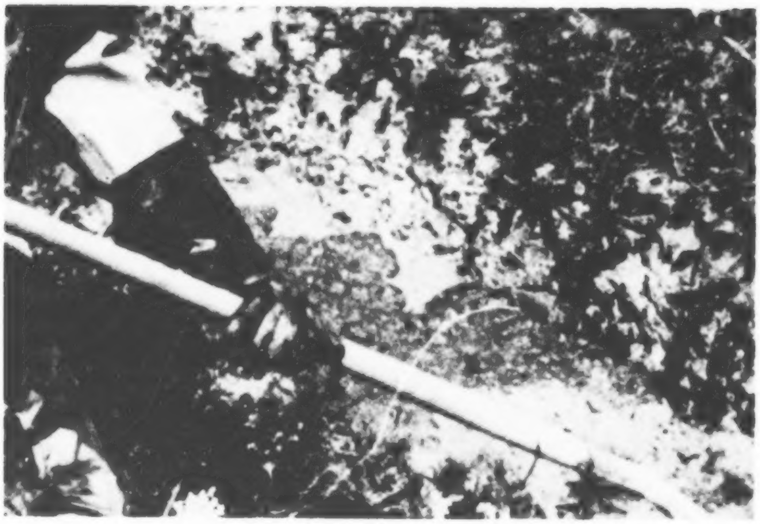


Figure 22A SLOW REACTION WHICH OCCURS WHEN LIME IS SPREAD ON TOP OF ACID-FLY ASH SLURRY

Figure 22B CLOUD FORMED BY INTENSE REACTION THAT OCCURS WHEN LIME LAYER IS RAKED INTO ACID-FLY ASH SLURRY BELOW

As the lime was raked into the acid fly ash slurry (Figure 22B), the accelerated reaction was so intense that a dense cloud formed in the ditch above the newly formed froth. Just prior to this experiment, a thunderstorm had saturated the Bethany site. The cloud probably consisted of water condensed out of the air on condensation nuclei that were generated by the reaction. Tiny sulfuric acid droplets may have been ejected into the air by breaking of bubbles in the heavy froth that was formed. The bubble breaking mechanism is a well known source of sea salt nuclei that predominate in maritime atmospheres. Regardless of the source of the cloud, it is evidence of the energetic reaction that occurred wherever fresh limestone was mixed into the acid slurry. When the reaction subsided, the cloud disappeared. When the slurry was raked without the addition of fresh lime, the cloud did not form.

This experiment was completed by gradually mixing 950 pounds of lime into the acid slurry over a 3.5 hour period. In the latter portion of the experiment water was mixed in with the lime and acid slurry to help drive the reaction to completion. In the final stage, slaked lime was mixed into the slurry to raise the pH to 8. The slurry was then shoveled into 55 gallon drums and the residue washed into the excavation below.

8. IMMOBILIZATION OF HEAVY METAL SPILLS ON LAND. Solutions of heavy metals can be immobilized on the surface by using any of the techniques described earlier; i.e., by congealing the solution with the universal gelling agents or absorption with fly ash or portland cement. Whatever fraction of the solution that has percolated into the soil is unaffected by these procedures, however. It was postulated that this material could be immobilized by application of sodium sulfide to the contaminated soil in order to convert the soluble salt to an insoluble sulfide. Heavy metal sulfide particles formed underground should be completely immobile except by erosion of the land surface.

To test this concept, 55 gallons of 5% $MnSO_4$ solution were spilled in each of the two 1% grade ditches at such a slow rate that all of the liquid soaked into the ditch bottom. One of the ditches was then treated with sodium sulfide using a 3.5 gallon garden sprayer. Fifty-five-gallon drums of water were then spilled rapidly at the head of each ditch and samples collected at the outfall about 10 seconds after passage of the leading edge of the surge flow. A steady flow was then maintained in the two ditches between periodic surge flows which were continued for the next 24 hours.

At the conclusion of the experiment, the water collected in the 12-foot-diameter pools contained 72 ppm and 6 ppm of dissolved Mn in the control and treated experiments, respectively. These numbers correspond to 10% and 1% of the total spilled material in the two ditches. The remainder of the metal was presumably trapped in the soil.

The experiment demonstrated conclusively that the treatment can significantly decrease the transport of spilled heavy metals to water-courses in subsequent surface runoff.

If the sodium sulfide treatment is used for treatment of land spills, it must be recognized that significant overtreatment may be necessary due to formation of sulfides of other competing metals already in the soil.

9. LOGISTICS AND COST OF IMMOBILIZATION PROCEDURES. Considering the wide variety of potential applications, treatment procedures and materials for immobilization of hazardous chemicals, it was not surprising that numerous possibilities exist for preparations to implement these techniques. At the state of development of the immobilization concept up to the end of this program, it was not appropriate to perform an exhaustive operational analysis of possible use concepts and associated preparation requirements and costs. Investigations, therefore, were limited, and intended only to provide sufficient information to generate an opinion as to the eventual practicability of the concept. For this study, use of the universal gelling agent was considered and the following assumptions made.

1. To be effective, attempts to seal leaking containers should be made within half an hour of the occurrence of the spill-producing accident so that small-scale local supplies and equipment are required.
2. To be effective, immobilization procedures for materials that are already on the surface should be initiated within a few hours after the occurrence of the spill.

The only practical concept visualized for maintaining local supplies of the universal gelling agent available for sealing leaky containers is to provide such supplies and equipment to either local fire departments or local law enforcement agencies. It is anticipated that equipment similar to dry chemical fire extinguishers with specially designed nozzles suitable for ejecting a narrow stream of gelling agent five to ten feet from the operator can be developed for this purpose. Judging from the cost of existing fire extinguishers, such equipment could be procured in quantity for under $100/unit. Ten thousand local organizations could then be equipped for a cost of $1,000,000.

The requirements for distribution of sufficient equipment and supplies for treatment of material on the surface is substantially more complex and must be considered on a regional basis. The distribution of caches located in Nevada, for example, need not be as dense as in the industrial regions of the northeast. Delivery of equipment and supplies from the cache to a spill in metropolitan areas must almost necessarily be by truck. In rural areas, delivery and direct dispersal from helicopters would be advantageous in many cases. Packaging problems are significantly different in the two cases.

Without attempting to solve these problems, it was assumed that as many as 200 sites throughout the country might be equipped and supplied for immobilizing spilled chemicals with the universal gelling agent and that delivery would be accomplished with ground transportation.

The following additional assumptions were made. Each site is supplied with 10,000 pounds of universal gelling agent (to provide a capability for treating 20,000-pound to 50,000-pound spills, depending on the chemical) packaged in 200 plastic-lined cardboard drums that are permanently stored on 20 warehouse pallets for ready loading on trucks. The 50-pound drums were selected to permit handling by one man in the field. Delivery equipment would include two modified sand blasters, one air compressor, and ten aluminum shovels. Protective clothing and gas masks for ten workers were also assumed at each site.

Assuming a price of \$2.00/lb. as an upper limit (slightly more than paid for our mix procured in experimental quantities), the outlay for the gelling agent would be \$20,000 per site. At the projected price of \$.50/lb., this cost could be as low as \$5,000. The following unit prices are appropriate for other equipment and supplies: drums, \$1.50; pallets, \$4.00; sand blasters, \$100.00; compressors, \$5,500.00; shovels, \$5.00; complete set of protective clothing, \$17.00; and gas masks, \$45.00. Cost per site for these items, plus \$300.00 for miscellaneous items not considered, would be \$7,000.00 Assuming \$2.00/lb. for the 200 sites throughout the country, this amounts to \$1.5 million for the gelling agent; cost per site would be \$27,000. Total cost for the 200 sites would be \$5.5 million. To this should be added the \$1 million for equipping 10,000 fire departments for sealing split containers.

In our opinion, these costs for preparation for immobilization of spilled hazardous chemicals are not excessive. The cost of training personnel, storing materials, and administering the program has not been considered. Certainly, further development of the concepts for immobilization of spilled materials is warranted.

Section 10

DETECTION AND MONITORING

For the effective treatment of spills of hazardous material, it is imperative that the spill be detected and identified rapidly and treated while it is concentrated. Rapid detection makes it possible to discover a spill before it is dilute and to reduce damage from the spill by means of localized treatment, impoundment and closing of municipal water intakes. A concentrated spill is easier to treat than a dilute spill and fewer biotae (including humans) are exposed to the spilled and treatment chemicals. If and when a spill occurs, the geographical extent and concentration of the spilled material must be monitored during the course of the treatment. Delineation of the amount and extent of untreated material permits cost-effective treatment and limits the exposure of the environment to excesses of the treatment chemicals.

For many spills, anticipation is impossible and early detection depends on the report of the person responsible for the spill or on environmental signs which are obvious to untrained observers (gross changes in color, odor, fish behavior, etc.). On the other hand, in certain probable spill locations, such as harbors and industrial rivers, arrays of automatic detectors could be cost-effective. To maximize the ratio of spill damage prevented to instrumentation cost, such detectors should react to a wide spectrum of possible pollutants, as do pH indicators, which respond to spills of acids, bases, and chemicals (such as liquified chlorine and ammonia) which form acids or bases when mixed with water. Furthermore, to be suitable for such applications, instrumentation must require little maintenance and be resistant to deterioration in the hostile environment characteristic of sewers and industrial rivers.

The requirements on equipment and methods for monitoring the extent of a spill and the progress in its treatment are somewhat different. Such equipment does not require the same degree of environmental immunity as the detection instruments since it need be deployed only during the treatment of a spill and need survive only a few hours of environmental exposure. Temporary deployment also obviates the need for extended periods of maintenance-free operation and permits rather rapid expenditure of consumables, e.g., indicator chemicals. Since an operator can be deployed with the equipment, automatic operation is not necessary and an operator is available for interpreting the equipment outputs. Finally, a few highly portable instruments can cover a rather wide area os possible pollution sites; so cost is not quite so critical as for the detection devices. On the other hand, monitoring equipment must give semiquantitative results -- at the very minimum, an indication of the endpoint of the spill-treatment titration -- and should provide a fairly specific indication of the nature of the spilled material. Furthermore, although an operator is available, he, in general, will not be skilled in chemistry or electronics; so the instrument should require only the normal observational skills of the average person, as does a colorimetric indicator.

During 1971-72 a study was undertaken to select methods and instrumentation that are commercially available or could be quickly developed to meet the aforementioned detection and/or monitoring equipment criteria, with major emphasis on applications to the detection and monitoring of spills into watercourses. A wide range of chemical and physical phenomena were explored in this effort, as described in detail in a separate volume of this report. Electrical conductivity was found to be highly effective in detecting the presence and measuring the extent of untreated ionic solute spills but was essentially worthless in indicating the effectiveness of the treatment. Commercial pH probes and certain other specific ion probes proved to be highly effective in detecting and measuring spills of acids, bases, and metallic salts and in monitoring the effectiveness of their treatment. Volatile organics triggered indications from commercial catalytic combustion sensors while less volatile organics were detected with a multicolor transmissometer. Colorimetric indicators proved to be extremely helpful and were used both in a spill detection kit designed for use by firemen and in an automatic "cyclic colorimeter," which uses modulation of indicator injection to reduce its sensitivity to turbidity and fouling. Colorimetric indicators were not reliable when added to a water body (e.g., as a stripe sprayed from a low flying airplane) to delineate the extent of the spilled material. Other experiments indicated the effectiveness of dyes as spill tracers and of the sense of smell as a spill detector. One of the most significant outcomes of the effort was the development of a spill detection kit containing a conductivity meter, pH indicator, odor samples, and colorimetric reagents geared to the prescribed spill treatments. This kit has been proven effective in tests involving volunteer firemen as operators.

Details of the instrumentation portion of this project are presented in a separate report.

Section 11

BIOASSAY STUDIES

Bioassay experiments followed the procedures recommended in Standard Methods, 13th Edition. The water pH, temperature, level of dissolved oxygen, exposure to ambient light, and concentrations of toxicant were all controlled and recorded, as well as additional parameters of the water quality including its alkalinity and hardness. Water quality data are listed in Table 16. The test temperature for all of our experiments was 60°F ±1°F and the lighting cycle was adjusted to produce 12 hours of simulated daylight and 12 hours of darkness.

The LD_{50} values for the six major compounds of interest in this study, over a seven day exposure period, were determined. In addition, observations were made of the minimum concentration of each substance which produced any observable untoward effects and/or deaths of the test organisms. Numerous well-characterized controls were included in all bioassay tests.

The selected test organisms were the fathead minnow, *Pimephales promelas promelas*, (acclimated to the test water for 24 to 48 hours prior to each experiment), algae, *Chlamyclomonas reinhardtii*, and plants, *Ceratophyllum demersum*. During the experiments, daily records were kept of fish behavior and fish deaths. Upon the death of any fish, it was immediately removed from the assay tank.

A brief summary of the large amount of data generated in these bioassay tests is provided in the following tables and graphs. Table 17 and Figures 23 through 25 report the findings after challenging both fish and algae with 10 ppm concentrations of nine chemicals of major interest in this program. Recognizing that there was a natural decay rate of each of these chemicals during the assay procedure, especially due to continuous aeration of the system, data were also collected on the dissipation rates which were encountered. Figure 26 plots these data.

Tables 18 and 19 provide information on the time elapsed before observable detrimental effects were encountered with lower than 10 ppm concentrations of each nominally hazardous chemical. The approximate LD_{50} values are also reported.

One of the major tasks of the bioassay program was to determine the potential secondary environmental consequences of application of our recommended countermeasures. Chief among the countermeasures for soluble hazardous chemicals in water has been treatment with activated carbon. Thus, both powdered and granular activated carbon with adsorbed test pollutant (phenol and acrylonitrile) were used as a "secondary pollutant" challenge in our bioassay system. Tables 20 21 and 22 document the findings that adverse secondary effects were indeed observed after exposure of fish to the pollutant-loaded carbon sediments, whether in powdery or granular form. The bulk water concentrations of pollutants were well below the levels found, in the preliminary series of tests, to cause adverse

Table 16

THE CHEMICAL ANALYSIS OF TEST WATER SOURCE (mg/1)

PARAMETER	METHOD*	TEST WATER
TOTAL HARDNESS	122B	132
CALCIUM	110C	95
MAGNESIUM	127B	37
POTASSIUM	147A	1.2
IRON	124D	0.220
COPPER	119A	0.025
ZINC	165A	0.015
CADMIUM	109A	nil < 0.01
CHROMIUM	117B	nil < 0.01
NICKEL	129A	nil < 0.01
LEAD	125B	nil < 0.05
ALKALINITY	102	90
TOTAL SUSPENDED SOLIDS	148B	14
TOTAL SOLIDS	148B	174
SULFATE	156C	25
NITRATE	133A	0.13
NITRITE	134	0.0230
AMMONIA	132B	0.07
PHENOL	U.V. Absorption	nil < 0.25
CHLORINE	114A	nil < 0.01
CHLORIDE	Specific Ion Electrode	58
FLOURIDE	121C	1.09
CYANIDE	Specific Ion Electrode	nil < 0.5
pH	-	7.34
DISSOLVED OXYGEN	218B	9.85

*Section as refers to Standard Methods, 13th ed.

Table 17

MORTALITY DATA IN PERCENT DEATHS OF MINNOWS WITH TIME AFTER EXPOSURE TO 10 ppm OF NINE CHEMICALS AT 60°F

	CONTROL	CHLORINE WATER	10 ppm H_g^{++} (H_gCl_2)	ACETONE CYANOHYDRIN	10 ppm Cd^{++} ($Cd\ Cl_2$)	AMMONIUM HYDROXIDE	PHENOL	10 ppm Cr^{+6} ($Na_2Cr_2\ O_7$)	ACRYL-ONITRILE	METHANOL
1 HOUR	0%	86.7%	1.7%	0%	0%	0%	0%	0%	0%	0%
2 HOURS	0%	100%	96.7%	13.3%	0%	1.7%	0%	0%	0%	0%
3 HOURS	0%	-	100%	23.3%	0%	5.0%	0%	0%	0%	0%
6 HOURS	0%	-	-	43.3%	3.3%	3.3%	0%	0%	0%	0%
1 DAY	0%	-	-	93.3%	76.6%	45%	0%	0%	0%	0%
2 DAYS	0%	-	-	100%	93.3%	45%	0%	0%	0%	0%
7 DAYS	0%	-	-	-	93.3%	46.7%	3.3%	0%	0%	0%
14 DAYS	0%	-	-	-	93.3%	50%	6.7%	0%	0%	0%

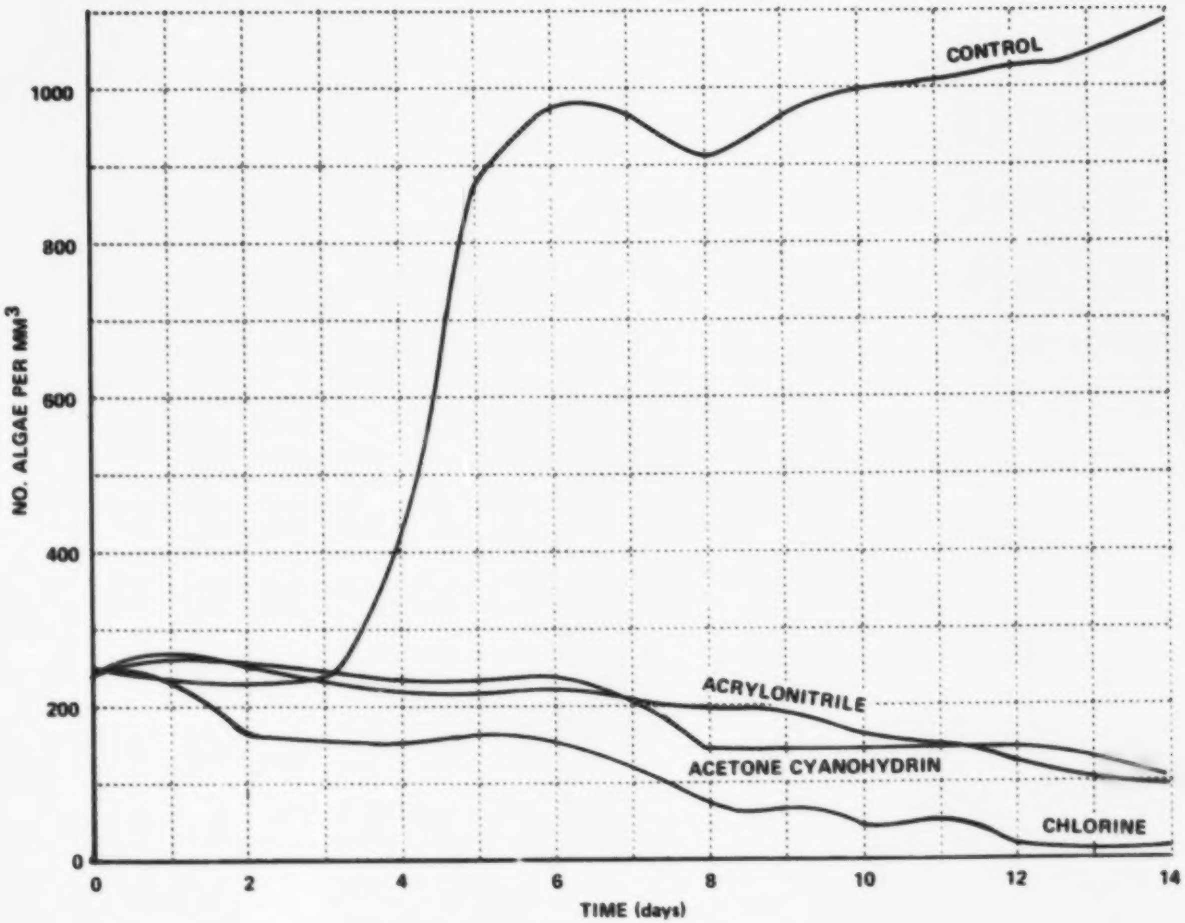


Figure 23 ALGAE GROWTH CURVES FOR ACETONE CYANOHYDRIN ACRYLONITRILE AND CHLORINE TESTS AT 10 ppm (60°F ± 1°F)

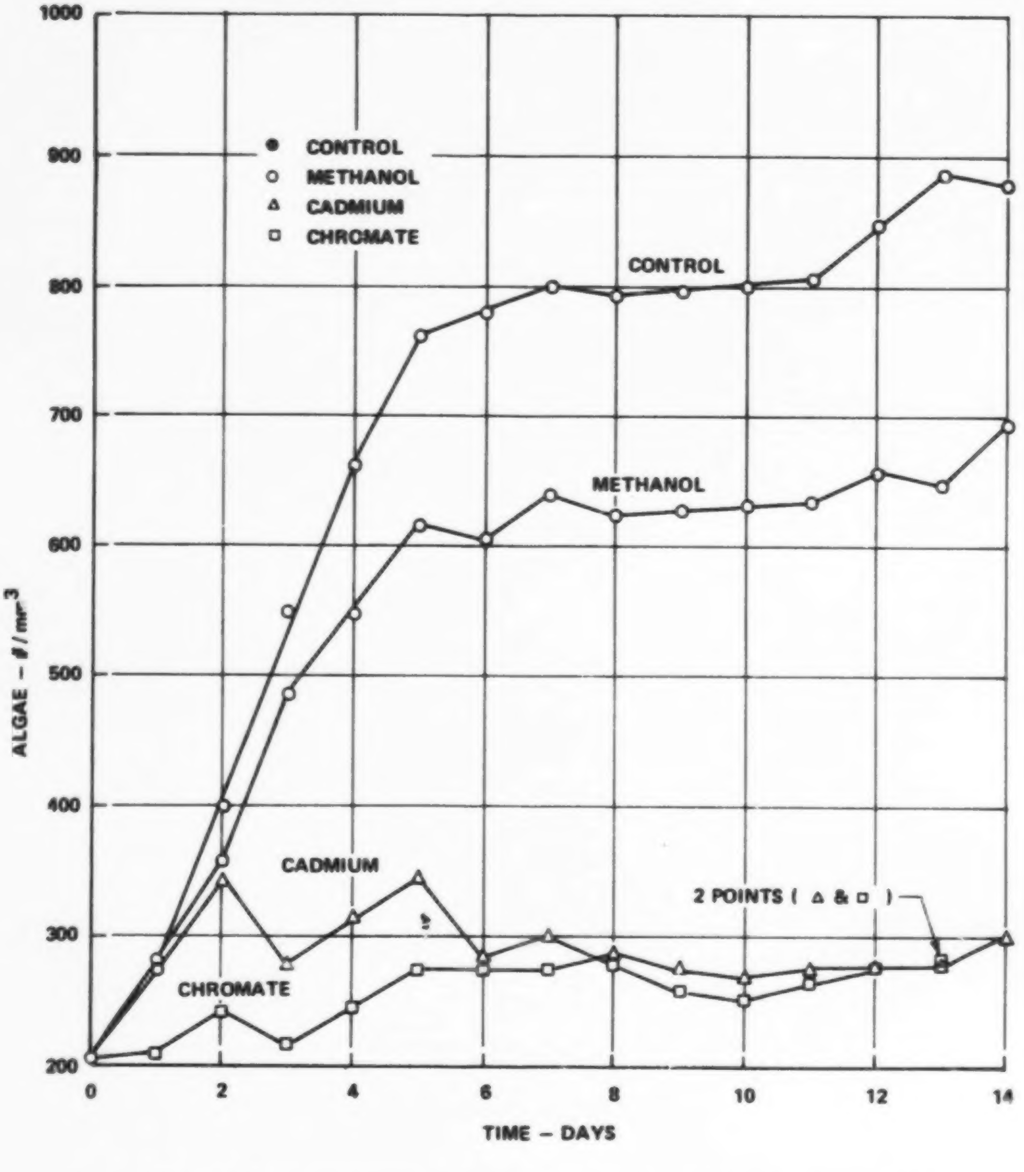


Figure 24 ALGAE GROWTH RATE WITH TIME AFTER EXPOSURE TO 10 ppm METHANOL, CADMIUM, AND CHROMATE

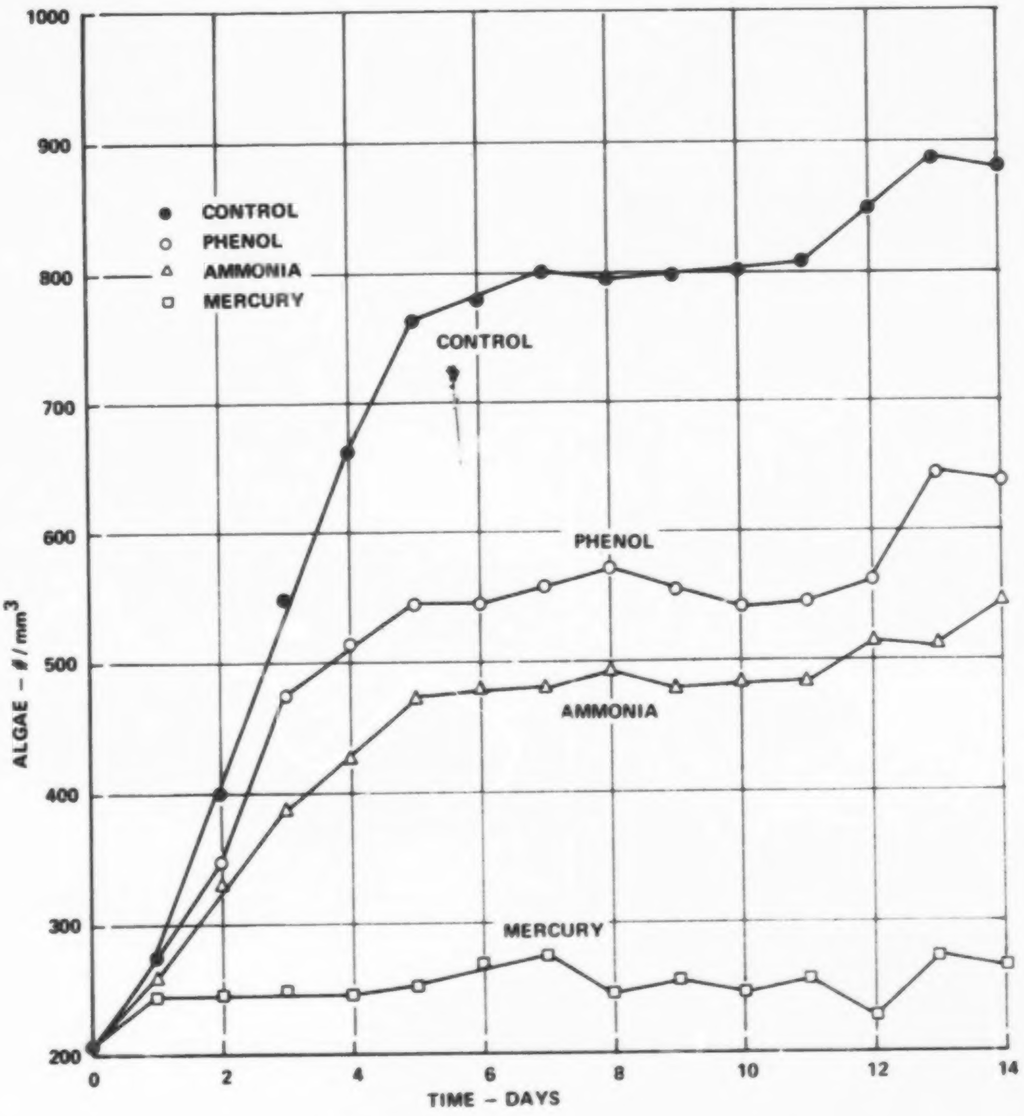


Figure 25 ALGAE GROWTH RATE WITH TIME AFTER EXPOSURE TO 10 ppm PHENOL, AMMONIUM HYDROXIDE, AND MERCURY

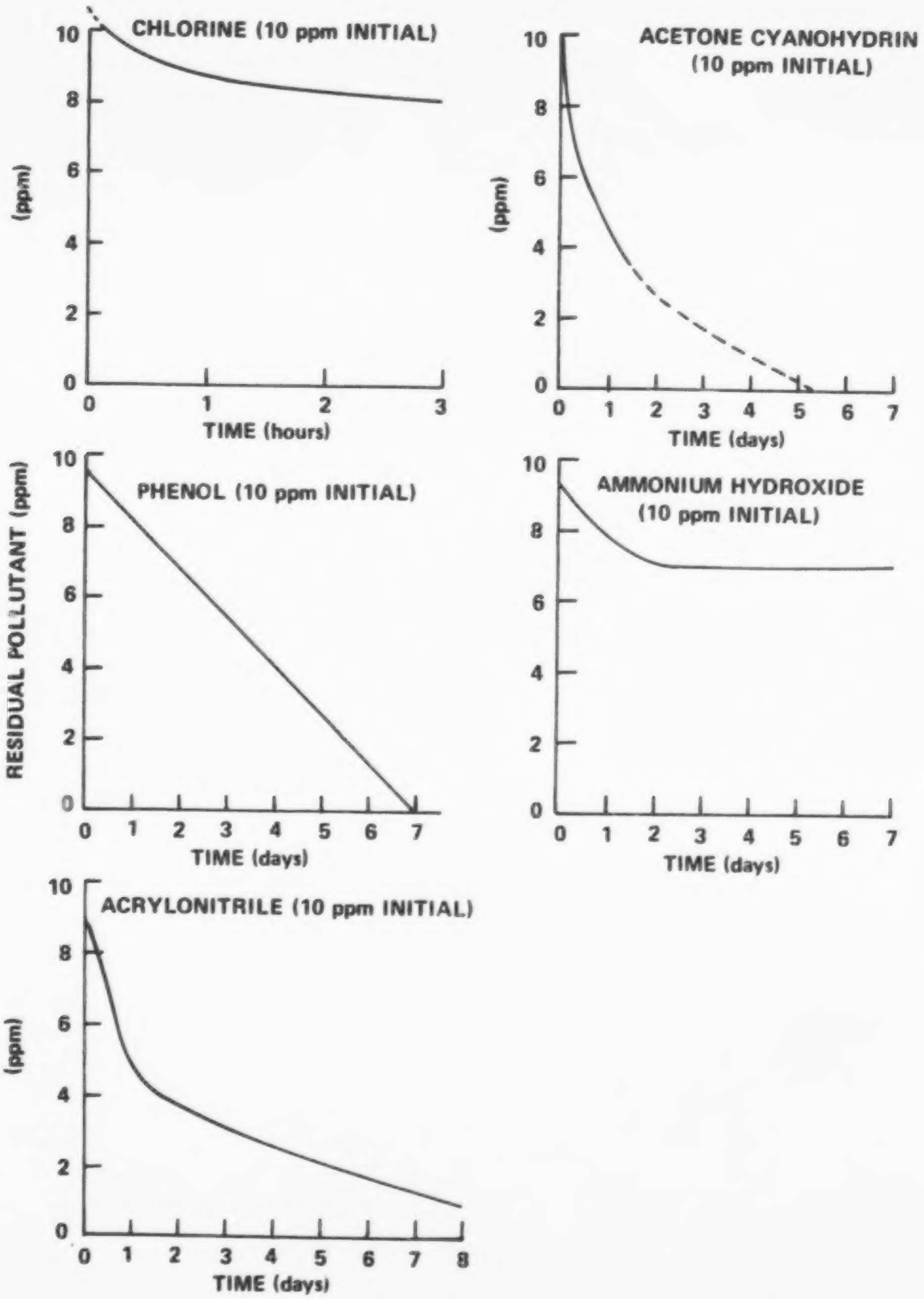


Figure 26 DISSIPATION OF VOLATILE POLLUTANTS (ppm) WITH TIME IN AN AERATED SYSTEM

Table 18

SAFE AND LETHAL CONCENTRATIONS OF POLLUTANTS INCLUDING THE LD^{50} FOR FATHEAD MINNOWS AND FOR A 7-DAY PERIOD OF OBSERVATION (ppm)

POLLUTANT	MAXIMUM SAFE LEVEL	MINIMUM LETHAL DOSAGE	LD_{50}
ACETONE CYANOHYDRIN	0.5	1.0	1.42
ACRYLONITRILE	20	(40)	30
AMMONIUMHYDROXIDE	5	7.5	10
CHLORINE	0.05	0.1	0.165 (4 day)
METHANOL	10,000	15,000	17,800
PHENOL	10	40	56.5

Table 19

LENGTH OF TIME BEFORE PHYSICAL EFFECTS AND/OR DEATHS WERE OBSERVED

POLLUTANT	EFFECTS OBSERVED AT:	DEATHS OCCURRED AT:
METHANOL		
10,000	1 hour - 24 hours	None
15,000	1 hour - 24 hours	30 hours only
20,000	15 min. - 24 hours	24 hours - 48 hours
25,000	15 min. - 24 hours	2 hours - 24 hours
30,000	Immediately	3 hours - all dead
50,000	Immediately	30 min. - all dead
ACRYLONITRILE		
10	None	None
20	None	None
40	24 hours and after	5 days and after
80	6 - 24 hours	12 - 24 hours
100	6 - 24 hours	12 - 24 hours
ACETONE CYANOHYDRIN		
0.1	None	None
0.5	3 - 6 hours	None
1.0	30 min. - 24 hours	24 hours (20%)
1.25	1 hour - 24 hours	None
2.5	30 min. - 24 hours	3 - 24 hours (80%)
5.0	30 min. and after	1-1/2% - 24 hours (100%)
10.0	15 min. and after	2-1/2% - 24 hours (100%)
20.0	Immediately	1-1/2 hours (100%)
CHLORINE		
0.05	None	None
0.1	3 hours - 30 hours	24 hours - 48 hours (60%)
0.5	2 hours - 4 days	24 hours - 4 days (70%)
1.0	30 min. and after	3 hours - 8 hours (100%)
1.25	15 min. and after	2 hours - 6 hours (100%)
2.5	5 min. and after	1 hour - 4 hours (100%)
5.0	Immediately	30 min. - 1-1/2 hours (100%)
AMMONIUM HYDROXIDE		
1.25	None	None
2.5	None	None
5.0	None	None
7.5	6 hours - 5 days	24 hours - 5 days (60%)
10	None observed	3 hours - 24 hours (50%)
20	None observed	45 min. - 75 min. (100%)
40	None observed	30 min. (100%)
PHENOL		
10	None	None
15	1 hour - 24 hours	None
20	15 min. - 48 hours	None
40	15 min. and after	48 hours - 6 days (30%)
80	10 min. and after	24 hours - 6 days (90%)
100	5 min. and after	24 hours - 6 days (80%)
150	Immediately	1 hour - 4 days (100%)
200	Immediately	1 hour - 3 days (100%)

Table 20

PERCENT SURVIVAL OF FISH WITH TIME DURING EXPOSURE TO A PHENOL-CARBON SEDIMENT (AQUA NUCHAR A; POWDERED CARBON)

TIME	PHENOL TEST	CONTROL
INITIAL - 5 DAYS	100%	100%
6 - 12 DAYS	96%	100%
13 - 21 DAYS	92%	100%
22 DAYS	88%	100%
23 DAYS	80%	100%
24 DAYS	72%	100%
25 DAYS	68%	100%
28 DAYS	68%	98%
29 AND 30 DAYS	68%	98%

Table 21

PERCENT SURVIVAL OF FISH EXPOSED TO PHENOL-CARBON SEDIMENT (GRANULAR CARBON)

TIME	AMOUNT OF PHENOL IN WATER	% SURVIVAL IN PHENOL	% SURVIVAL IN CONTROL
INITIAL	0.1 - 0.3 ppm	100%	100%
7 DAYS	nil < 0.10 ppm	95%	97%
15 DAYS	nil < 0.10 ppm	78%	86%
30 DAYS	0.9 ppm	45%	65%

Table 22

PERCENT SURVIVAL OF MINNOWS EXPOSED TO A SEDIMENT OF ACRYLONITRILE-GRANULAR CARBON AND SAND

TIME	% OF FISH SURVIVAL	DUPLICATE TEST	CONTROL
0-3 HOURS	100%	100%	100%
1 DAY	80%	100%	100%
2 DAYS	48%	100%	100%
3 DAYS	30%	-	100%
4 DAYS	0%	0%	100%

effects by themselves. Therefore, it was concluded that activated carbon with absorbed pollutants cannot be allowed to persist at the stream bottom in natural waterways supporting mixed biological communities.

Another countermeasure developed during the HASP program was the immobilization of hazardous liquid spills with a powdered gelling agent. Bioassay tests in which living organisms were challenged with gel-immobilized benzene and acrylonitrile showed that here, again, rapid adverse effects were noted (culminating in fish death). Thus, it is necessary that even gelled hazardous liquids be removed from biologically productive watercourses as rapidly as possible. On the other hand, it was noted that exposure of fish to high solids concentrations (ranging up to thick slurries of carbon in water with concentrations of 100,000 ppm) could, over short contact times, be tolerated by fish in the absence of a hazardous organic pollutant.

Another countermeasure developed under this program was the addition of sodium sulfide solutions to pollutant plumes of dissolved heavy metal salts on the theory that the precipitated metallic sulfide ores would be innocuous. Bioassay tests on this system indicated that the sodium sulfide itself, probably because of its very high natural pH, was also a toxic to varying degrees over long water contact times (60 days) and that the dissolved secondary sodium salts produced in the water column could also, on occasion, have adverse biological effects. These long term studies with sodium sulfide and the heavy metal sulfide precipitates also included exposure of a plant, the hornwart, in order to assess the potential deleterious effects on water plants. In some instances, severe deterioration of this plant was noted upon exposure to the supposedly inert heavy metal ores residing at the bottom of the test tanks. All of these findings are documented in Tables 23, 24, 25 and 26.

Recommendations for future study include providing the substantial amount of missing information on the relative toxicities of a greater variety of hazardous chemicals (as determined through static bioassay tests such as those reported here). It is also to be recommended that determinations be made of the tests organisms' (fathead minnows) ability to recover after a brief initial exposure to a high concentration plume of toxicant and to exposure of various toxicant levels in a continous flow system.

Table 23

ESTIMATES OF TOXICITY TO FISH OF VARIOUS METALS

METAL COMPOUND	TOXIC CONCENTRATIONS (ppm)	FISH USED	TYPE OF TEST
BARIUM Cl	50	SALMON	72 HOUR
NO_3	200	"FISH"	96 HOUR
CADMIUM Cl	0.9 (SOFT H_2O)	FATHEAD MINNOWS	96 HOUR
	5.0 (HARD H_2O)	FATHEAD MINNOWS	96 HOUR
NO_3	6	FUNDULUS	--
	0.3-7	STICKLEBACK	--
SO_4	1000	FISH	3 HOUR
CHROMIUM (+3)	5.2	TROUT	--
	1.2	STICKLEBACK	--
	40	MINNOWS	--
(Na) CHROMATE	300-400	FISH	--
(Na) DICHROMATE	60	FISH	--
(K) CHROMATE	75	FISH	--
COPPER Cl	3.3	FISH	24 HOUR
NO_3	0.18	FISH	--
SO_4	0.15	TROUT	INCIP. TOX. LEVEL
COBALT Cl	16	FUNDULUS	5 DAY
	10-15	STICKLEBACK	--
NO_3	15	FISH	--
MANGANESE Cl	300	FISH	--
CO_3	40	FISH	--
SO_4	500	FISH	--
NICKEL Cl	5	FISH	--
NO_3	1	FISH	--
SO_4	10-16	GOLDFISH	200 HOUR
Pb Cl	0.5	FISH	--
NO_3	10	FISH	--
SO_4	25	FISH	--
SILVER NO_3	0.04	FISH	--
ZINC Cl	15	FISH	--
NO_3	5.7	FISH	--
SO_4	3	FISH	--

Table 24

DATA ON THE TOXICITY OF Na_2S TO MINNOWS
(% DEATHS WITH TIME)

TIME	CONCENTRATION (ppm)									
	0	10	20	40	80	100	200	300	500	1000
INITIAL	0	0	0	0	0	0	0	0	0	0
0.25 HOURS	0	0	0	0	0	0	0	10%	60%	100%
0.5 HOURS	0	0	0	0	0	0	0	50%	100%	--
1.0 HOURS	0	0	0	0	0	0	80%	100%	--	--
1.25 HOURS	0	0	0	0	0	0	100%	--	--	--
3 HOURS	0	0	0	0	0	0	--	--	--	--
6 HOURS	0	0	0	0	0	0	--	--	--	--
24 HOURS	0	0	0	0	10%	20%	--	--	--	--
48 HOURS	0	0	0	10%	20%	30%	--	--	--	--
72 HOURS	0	0	0	10%	20%	30%	--	--	--	--
7 DAYS	0	0	0	10%	20%	30%	--	--	--	--
INITIAL pH (AVE)	8.33	8.93	9.14	9.50	9.95	-	-	11.42	11.70	11.15

Table 25

PERCENT DEATHS OF MINNOWS WITH TIME AFTER EXPOSURE TO NaCl, $NaNO_3$, & Na_2SO_4

DAYS	CONTROL	1000 ppm Na_2SO_4	1000 ppm $NaNO_3$	1000 ppm NaCl
1	0%	0%	20%	30%
2	0%	0%	20%	30%
3	0%	0%	20%	30%
4	0%	0%	20%	30%
5	0%	0%	20%	30%
6	0%	0%	20%	40%
7	0%	0%	20%	50%

Table 26

SUMMARY OF DATA FROM METAL PRECIPITATE TESTS

METAL PRECIPITATE TESTED	RANGE OF METAL CONCENTRATION IN TEST H_2O THROUGHOUT TEST (ppm)	EQUILIBRIUM CONCENTRATION OF METAL (ppm) FROM THE SOLUBILITY OF THE SULFIDE	TOXICITY RANGE TO FISH (FROM LITERATURE)	% SURVIVAL OF FISH AFTER 60 DAYS	CONDITION OF THE CERATOPHYLLIUM AT TERMINATION
CONTROL	-	-	-	95.4	HEALTHY AND WITH GREEN FOLIAGE
ZINC SULFIDE	0.01-1.20	5.0	0.3-15	100.0	HEALTHY AND WITH GREEN FOLIAGE
CADMIUM SULFIDE	0.005-0.70	1.0	0.01-7	98.0	NO LEAVES, ONLY A GREEN STALK
LEAD SULFIDE	0.35-0.67	0.8	0.1-25	94.0	HEALTHY AND WITH GREEN FOLIAGE
COOPER SULFIDE	0.05-0.30	0.2	0.01-3.3	92.0	20-30% WITH LEAVES
COBALT SULFIDE	2.4-7.0	3.0	7-16	80.0	HEALTHY AND WITH GREEN FOLIAGE
SILVER SULFIDE	nil<0.01	0.1	0.04	74.5	20-30% WITH LEAVES
NICKEL SULFIDE	2.9-8.15	2.4	0.08-16	41.0	DISINTEGRATED TO A PILE OF DEBRIS
BARIUM CHROMATE	3.0-4.5 (Ba^{+2}) 0.40-0.80 ($CrO_4^{=}$)	1.0	50-200 (Ba^{+2}) 75-400 ($CrO_4^{=}$)	53.0	HEALTHY
CONTROL	-	-	-	49.0	HEALTHY
MANGANESE SULFIDE	3.0-18.25	3.0	40-500	63.0	HEALTHY
CONTROL	-	-	-	61.0	HEALTHY

SECTION 12

MATHEMATICAL MODELING OF HAZARDOUS SPILLS AND SPILL TREATMENT

In the course of deploying treatment material for a hazardous chemical spill in a water body, it is desirable to understand and characterize two important phenomena: (1) the time rate of consumption of the pollutant as a result of treatment; (2) the spreading or dispersion of the pollutant throughout the fluid. Since these are extremely complex phenomena to examine in real life, it becomes necessary to resort to mathematical models to suitably reproduce the above phenomena. The primary objective of such models is to simulate a variety of spill and treatment phenomena and to thereby facilitate the prediction of whether treatment in certain cases is feasible or not.

Both types of modeling were considered on this program. In the subsequent subsections, we will describe first a mathematical model of activated carbon treatment for removal of pollutants from solution. This model, based on parameters which are readily determined in the laboratory for any carbon-pollutant system, is useful for describing the rate of decrease of pollutant concentration as a result of carbon treatment. The dispersion models developed on the program are described thereafter.

1. MATHEMATICAL MODEL OF ACTIVATED CARBON TREATMENT

For the purpose of developing the rate model for the adsorption of pollutant, it was assumed that at time zero, V liters of solution containing the contaminant A are contacted with M grams of activated carbon in tea bags. Furthermore, it is assumed that the overall rate of uptake of A by the carbon depends on the following three physical steps.

1. Diffusion of A, from the bulk solution, through a very thin film of relatively stagnant solution surrounding the carbon particles.

2. Diffusion of A through the internal pores of the activated carbon particles.

3. Physical adsorption of A on an active site within the carbon particles.

In treating Steps 1 and 2, very simple rate equations are used, and temperature and concentration gradients within the external film and within the carbon particles are not taken into account. Thus, film and pore diffusion mechanisms (Steps 1 and 2) are treated as a single diffusional resistance. With these assumptions, the appropriate rate of depletion of A via film and pore diffusion is given by:

$$R_f = -\frac{dC_a}{dt} = k_f\ (C_a - C_{as}) \qquad (1)$$

where

R_f = rate of diffusional depletion of A, $\frac{\text{mg A}}{\text{liter-hr}}$

C_a = concentration of A in bulk solution, $\frac{\text{mg A}}{\text{liter}}$

C_{as} = concentration of A in pore solution within carbon particle, $\frac{\text{mg A}}{\text{liter}}$

k_f = diffusional transfer coefficient, hr^{-1}

t = time, hr

The third step, namely, physical adsorption of A on an active site within the carbon particle, can be well represented by the following reversible second-order reaction:

$$\left[\begin{array}{l}\text{A in pore solution with-}\\\text{in carbon particle}\end{array}\right] + \left[\begin{array}{l}\text{Available active}\\\text{sites within}\\\text{carbon}\end{array}\right] \rightleftharpoons \left[\begin{array}{l}\text{Adsorbed complex}\\\text{on active sites}\end{array}\right]$$

i.e.,

$$[\text{A}] + [\text{Sorbent}] \rightleftharpoons [\text{A}\cdot\text{Sorbent}] \qquad (2)$$

Based on Equation (2) the net rate of uptake of A by adsorption on active sites within the carbon particles may be written

$$R_a = \frac{dq_a}{dt} = k_a\ C_{as}\ (Q - q_a) - K_d\, q_a \qquad (3)$$

where

R_a = net rate of adsorption uptake of A, $\frac{\text{mg A}}{\text{g carbon-hr}}$

q_a = concentration of A adsorbed on carbon surface, $\frac{\text{mg A}}{\text{g carbon}}$

k_a = adsorption rate constant, $\frac{\text{liters}}{\text{mg A-hr}}$

Q = ultimate adsorption capacity of carbon, $\frac{\text{mg A}}{\text{g carbon}}$

$(Q-q_a)$ = available adsorption capacity of carbon, $\frac{\text{mg A}}{\text{g carbon}}$

k_d = desorption rate constant, hr^{-1}

In writing Equation (3), it is assumed that the local adsorption at an active site is proportional to the liquid phase concentration within the particle C_{as} and the available adsorptive capacity $(Q-q_a)$. The desorption is assumed to be proportional only to the quantity of A adsorbed, q_a. Equation (3) may be put in an alternate form:

$$R_a = \frac{dq_a}{dt} = k_a \left[C_{as} \left(Q-q_a\right) - K q_a\right] \qquad (4)$$

where

K = equilibrium constant $\frac{k_d}{k_a}$, $\frac{\text{mg A}}{\text{liter}}$

We have thus far identified two rate expressions: the rate of film diffusion with pore diffusion of A from bulk solution to an active site as given by Equation (1) and the net rate of adsorption of A onto an active site as given by Equation (4). It is now necessary to combine these two rate expressions so that the unmeasurable quantity C_{as} is eliminated and an overall rate expression is obtained in terms of C_a, the measurable quantity. This is done by assuming that there is no continual accumulation of A in the film and the carbon interior but rather that all A transported by film and pore diffusion is taken up by adsorption within the carbon particle. This can only happen when the rates in Equations (1) and (4) are equal, and therefore

$$R = VR_f = MR_a \qquad (5)$$

where

R = overall rate of uptake of A, $\frac{\text{mg A}}{\text{hr}}$

(Note that the quantities of V and M in Equation (5) are used in order to satisfy the dimensional units on both sides of the equalities in Equation (5).)

Therefore, substituting Equations (1) and (4) into Equation (5) and eliminating C_{as}, the following overall rate expression is obtained:

$$R = \frac{-VdC_a}{dt} = \frac{C_a\,(Q-q_a) - Kq_a}{\dfrac{1}{Mk_a} + \dfrac{(Q-q_a)}{VK_f}} \tag{6}$$

If it is assumed that the quantity of A in the pore fluid and in the stagnant film is negligible, then q_a can be expressed as

$$\begin{aligned} q_a &= (C_{ao} - C_a)\,\frac{V}{M} \\ &= (C_{ao} - C_a)\,\varepsilon \end{aligned} \tag{7}$$

where

C_{ao} = initial concentration of A, $\frac{\text{mg A}}{\text{liter}}$

ϵ = V/M

Equation (7) says that the amount of A adsorbed on the carbon interior is equal to the amount of A depleted in the bulk solution. Substituting Equation (7) into Equation (6) finally yields

$$\frac{-dC_a}{dt} = \frac{C_a^{\,2} + AC_a + B}{\dfrac{1}{k_a} + \dfrac{1}{k_f}\,(C_a + C)} \tag{8}$$

where

$A = Q' - C_{ao} + K$

$B = -KC_{ao}$

$C = Q' - C_{ao}$

$Q' = Q/\varepsilon$

Equation (8) is the desired rate expression which describes the depletion of A in the bulk solution in terms of the bulk phase concentration C_a. There are also four physical parameters of interest in the above rate expression; namely, Q, K, k_a and k_f. The first two parameters, Q and K, are equilibrium parameters and may be determined as follows. At equilibrium, $\frac{dq_a}{dt} = 0$ and hence Equation (4) becomes

$$k_a \left[C_{as} (Q-q_a) - Kq_a\right] = 0$$

i.e.,

$$\frac{C_{as}}{q_a} = \frac{C_{as}}{Q} + \frac{K}{Q} \tag{9}$$

A known quantity of A can be stirred in a beaker with a known quantity of carbon for an extended period of time at the end of which equilibrium may be assumed to have been attained. At equilibrium, the bulk concentration C_a is the same as the pore concentration C_{as}; also, q_a is obtained by Equation (7). This is repeated for different concentrations of C_{ao} and carbon quantities M so that enough points are obtained for a plot of $\frac{C_{as}}{q_a}$ versus C_{as}. According to Equation (9), this plot should yield a straight line with slope $\frac{1}{Q}$ and intercept $\frac{K}{Q}$. Such a plot is shown in Figure 27 and the values of Q and K are determined as 154.288 and 14.387 $\frac{\text{mg phenol}}{\text{g carbon}}$, respectively.

The third parameter, k_a, would be expected to depend on the type of carbon used and also the solute A (as also would the first two parameters, Q and K). The fourth parameter, k_f, would largely depend on the physical environment such as the type and degree of agitation and local turbulence in the vicinity of the carbon particles. Parameters k_a and k_f would have to be determined by fitting the rate expression in Equation (8) to actual concentration vs time data obtained from controlled laboratory tests under different flow conditions.

The parameter k_a is best determined under conditions where resistance due to film transfer is expected to be the least, whereby all resistance to the transfer of pollutant from solution to carbon can be assumed to be due to adsorption only. Such a condition can be realized in a beaker in which phenol solution and loose granular carbon is vigorously agitated or stirred. In this manner of contacting, film transfer resistance $(\frac{1}{k_f})$ is negligible and Equation (8) reduces to

$$\frac{-dC_a}{dt} = \frac{C_a^2 + AC_a + B}{\frac{1}{k_a}} \tag{10}$$

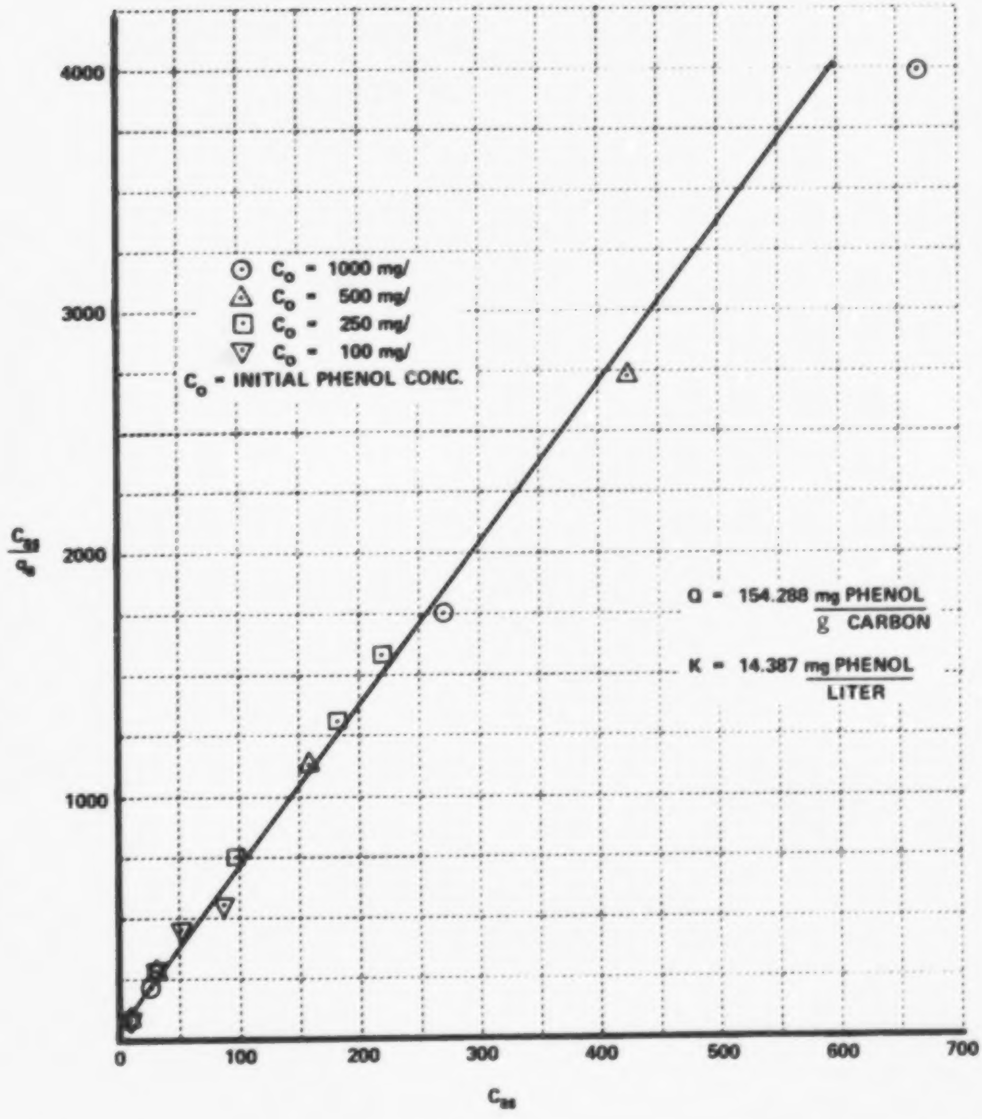


Figure 27 EQUILIBRIUM ADSORPTION OF PHENOL BY NUCHAR (8 x 30)

The parameter k_a in Equation (10) was therefore manipulated such that the concentration-time history predicted by Equation (10) was in close agreement with experimental results according to a least squares error criterion. The value of k_a determined by such a fit was found to be $0.002167 \frac{\text{liters}}{\text{mg phenol-hr}}$. Figure 28 shows the close fit obtained between model and data.

Since the adsorption rate constant k_a depends on a phenomenon occurring largely within the carbon, it will always be constant for a given carbon and pollutant regardless of how the carbon is deployed (tea bags or otherwise) or the external physical environment in the vicinity of the carbon particles. In direct contrast, the film transfer coefficient, k_f, depends almost entirely on the local turbulence, mixing and agitation in the vicinity of the carbon particles. Therefore, in evaluating k_f, attention must be paid to the kind of flow situation at hand.

In the estimation of k_f, channel tests were used to generate concentration vs time data. These data were obtained at different flow velocities, and k_f was determined for each flow velocity such that C_a vs t as predicted by Equation (8) was in close agreement with experimental channel data.

Figure 28 shows concentration-time values derived from Equation (8) as compared with experimental data. There are three sets of channel data presented in Figure 29 ; these are at flow velocities of 0, 0.5, and 1.0 ft/sec. In each case, the carbon dosage is 250 mg/liter. The 0 ft/sec data were actually generated in an unstirred beaker of 250 mg/liter phenol solution treated with a 10x dose of carbon in a tea bag. Examination of Figure 29 shows that the experimental data for each run (0, 0.5, and 1.0 ft/sec) may be well represented by the rate expression in Equation (8). The calculated curves generally fit the data in a satisfactory manner. Also, the film transfer coefficient increases with increase in flow velocity, which is to be expected.

The results of the parameter estimation of the treatment model are summarized in Table 27.

2. CONCLUDING REMARKS

Mathematical modeling is of great interest in that it furthers the understanding of spill dispersion and treatment, and displays in considerable detail the interactions between various parameters of interest. More importantly, perhaps, models are potentially important tools in aiding practical decisions. In the next subsection, we discuss the modeling of the spill dispersion and the treatment of spills. The actual coupling of these two models occurs via Equation (11) when the R(C) term is added. However, from the complex nonlinear form of R(C) as can be seen in Equation (8), no simple analytical solution (as in Equation 12)) is possible. The only way to obtain solutions is by numerical techniques implemented on a computer. Furthermore, sufficiently fine resolution may require thousands of points of storage capacity and this figure is then to be multiplied by the number of elements (flow components, stream depth, and so forth) pertinent to the model. The finer the spatial resolution, the smaller

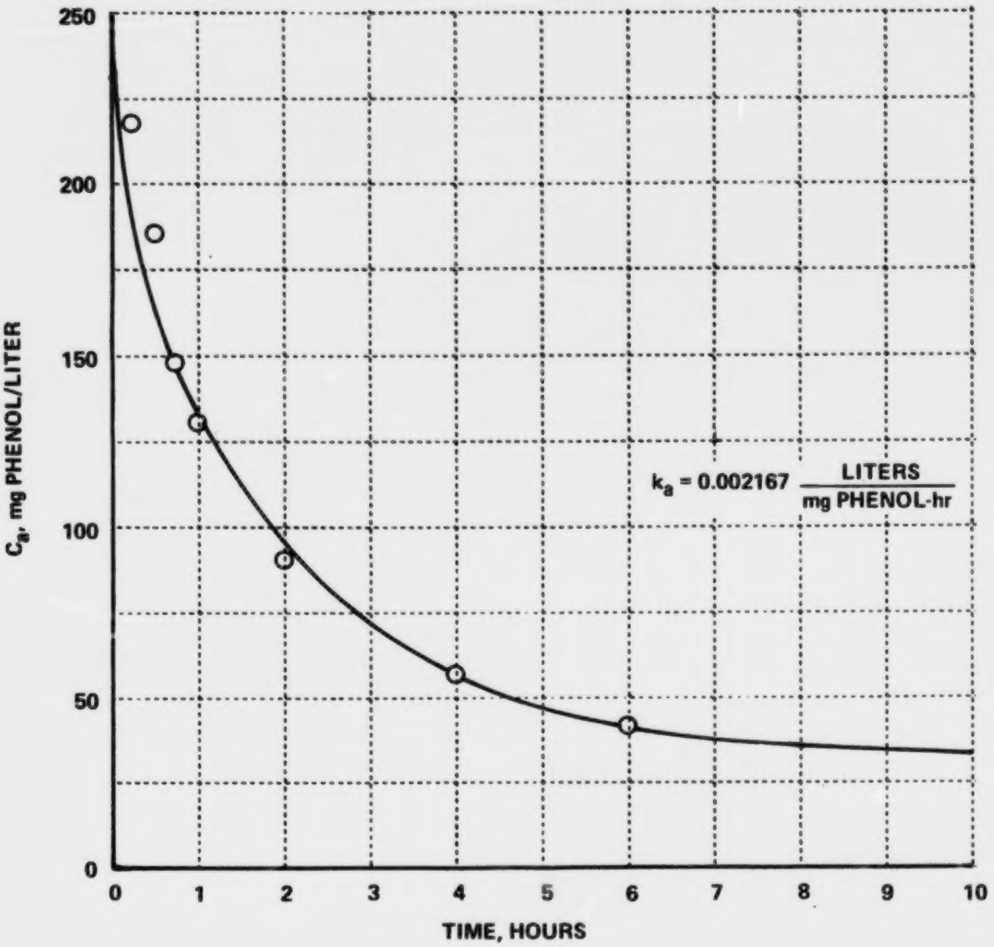


Figure 28 CONCENTRATION-TIME VALUES DERIVED FROM EQUATION 8 (CURVE) COMPARED WITH EXPERIMENTAL DATA (POINTS)

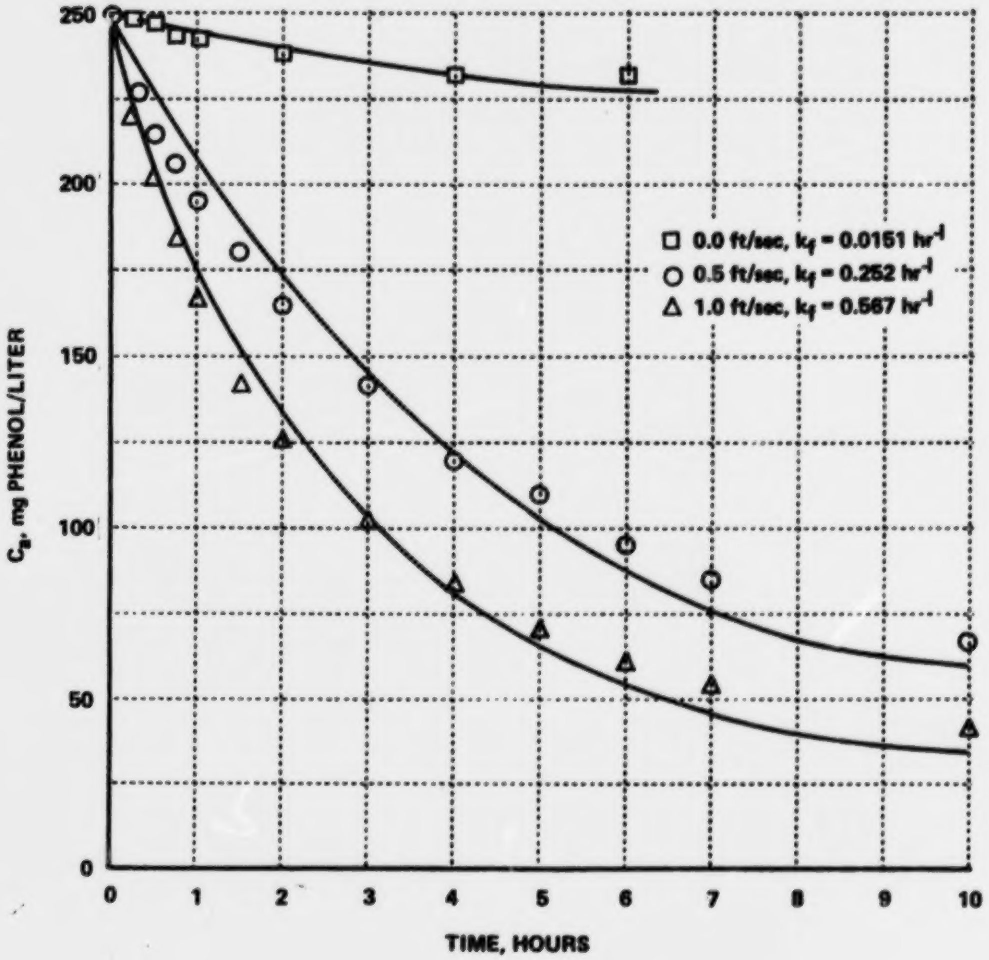


Figure 29 CONCENTRATION TIME VALUES DERIVED FROM EQUATION 4 (CURVES) COMPARED WITH EXPERIMENTAL CHANNEL DATA (POINTS)

Table 27

SUMMARY OF PARAMETERS ESTIMATED IN TREATMENT MODEL (PHENOL-NUCHAR 8 x 30)

PARAMETER	ESTIMATED VALUE	UNITS
Q	154.288	$\frac{\text{mg Phenol}}{\text{gm Carbon}}$
K	14.387	$\frac{\text{mg Phenol}}{\text{liter}}$
k_a	0.002167	$\frac{\text{liters}}{\text{mg Phenol-hr}}$
k_f at 0.0 ft/sec	0.0151	1/hr
k_f at 0.5 ft/sec	0.252	1/hr
k_f at 1.0 ft/sec	0.567	1/hr

the time step permissible without violating computational stability. All this obviously calls for computers with vast storage capacities and speedy computational abilities. However, this certainly does not present any obstacle since rapid advances in computer design have made such computation possible.

The major limitation is physical in nature. As discussed later, the incomplete knowledge of dispersion coefficients hampers realistic dynamic simulation of the dispersion model. Also, in the case of the treatment model, various carbon-pollutant combinations must be analyzed to determine constants such as Q, K and k_a. These physical coefficients must be established in order that the simulation of hazardous spills and their treatment is not left to guesswork and speculation. These various constants and coefficients could be set up in some form of unified information retrieval system such that for a given spill in a specific water body all the necessary parameters are made available to the individual(s) who are faced with the decision of where and when to treat a given spill. It is in this capacity that the greatest benefit from mathematical models will be realized.

3. MATHEMATICAL MODEL OF POLLUTANT DISPERSION IN FLOWING STREAMS

The equation which governs the distribution of a pollutant in a continuum is the classical mass conservation equation

$$\frac{\partial c}{\partial t} + u\frac{\partial c}{\partial x} + v\frac{\partial c}{\partial y} + w\frac{\partial c}{\partial z} = K\frac{\partial^2 c}{\partial x^2} + K_y\frac{\partial^2 c}{\partial y^2} + K_z\frac{\partial^2 c}{\partial z^2} - R(c) \qquad (11)$$

where

C = concentration of the pollutant

u,v,w = velocities of the fluid in x, y, and z directions

K_x,K_y,K_z = turbulent or eddy dispersion coefficients, respectively

x,y,z = longitudinal, lateral and vertical coordinates, respectively

R (C) = rate at which pollutant is being consumed

t = time

At present, we shall confine ourselves to Equation (11) without the term R(C). We shall discuss this term in more detail.

The solution to Equation (11) (without R(C)) is

$$C = \frac{K}{t^{3/2}} \exp \left\{ -\frac{1}{4t} \left[\frac{(x - ut)^2}{K_x} + \frac{y^2}{K_y} + \frac{z^2}{K_z} \right] \right\} \qquad (12)$$

where it is assumed that u is the only non-zero stream flow velocity and K is given by

$$K = \frac{M}{8\pi^{3/2}\sqrt{K_x K_y K_z}}$$

where M is the total mass of the spill.

Equation (12) represents the dispersion of material spilled at a specific point. An isoconcentration line would appear as an expanding ellipse whose center of symmetry is moving with a velocity u in the x direction. After a while the ellipse would begin to contract, representing the exhaustion of material within the boundary line. Figure 30 shows such elliptical contours at different time instants in a nonflowing water body. The contours represent the motion of the 10-ppm concentration boundary resulting from a 5000-gallon phenol spill, 100 meters from the shoreline. Note that after about 24 hours, the 10-ppm boundary has reached a maximum and begins to recede toward the shoreline. This example serves to illustrate the natural dilution process involved and also the order of magnitude of time and distance necessary for dilution.

The necessary computations were performed on a Model 9810 Hewlett-Packard desktop calculator, while the results were plotted via an associated Hewlett-Packard plotter. The Model 9810 can be card programmed for up to 2000 program steps. Equation (12), along with a portable calculator equivalent to the Model 9810, allows the user a great deal of flexibility in that "on-site" calculations can be made while the spill is still spreading downstream. Rapid checks can be made on the spread and location of the flowing spill since computation time is of the order of a few seconds.

The values of K_x, K_y, and K_z used in this example are typical or "ballpark" values for nonflowing fluids. In the case of moving fluids, the convective and turbulent eddy effects have a marked effect on the dispersion coefficients. The major drawback to a realistic simulation of the dynamic process is the incomplete knowledge of the turbulent transport processes. The dispersion coefficients, in general, vary both in space and time in a manner that is not well understood. The question of how these coefficients vary with flow and/or channel geometry needs to be investigated both experimentally and analytically to aid in the application of models to the prediction of spill behavior.

Until more complete information becomes available on representative values of dispersion coefficients for different types of water bodies under different conditions, it appears that some on-site adaptive prediction procedure will be required to provide the field worker with information needed for decision-making. Recognizing that the field worker needs information quickly but has no requirement

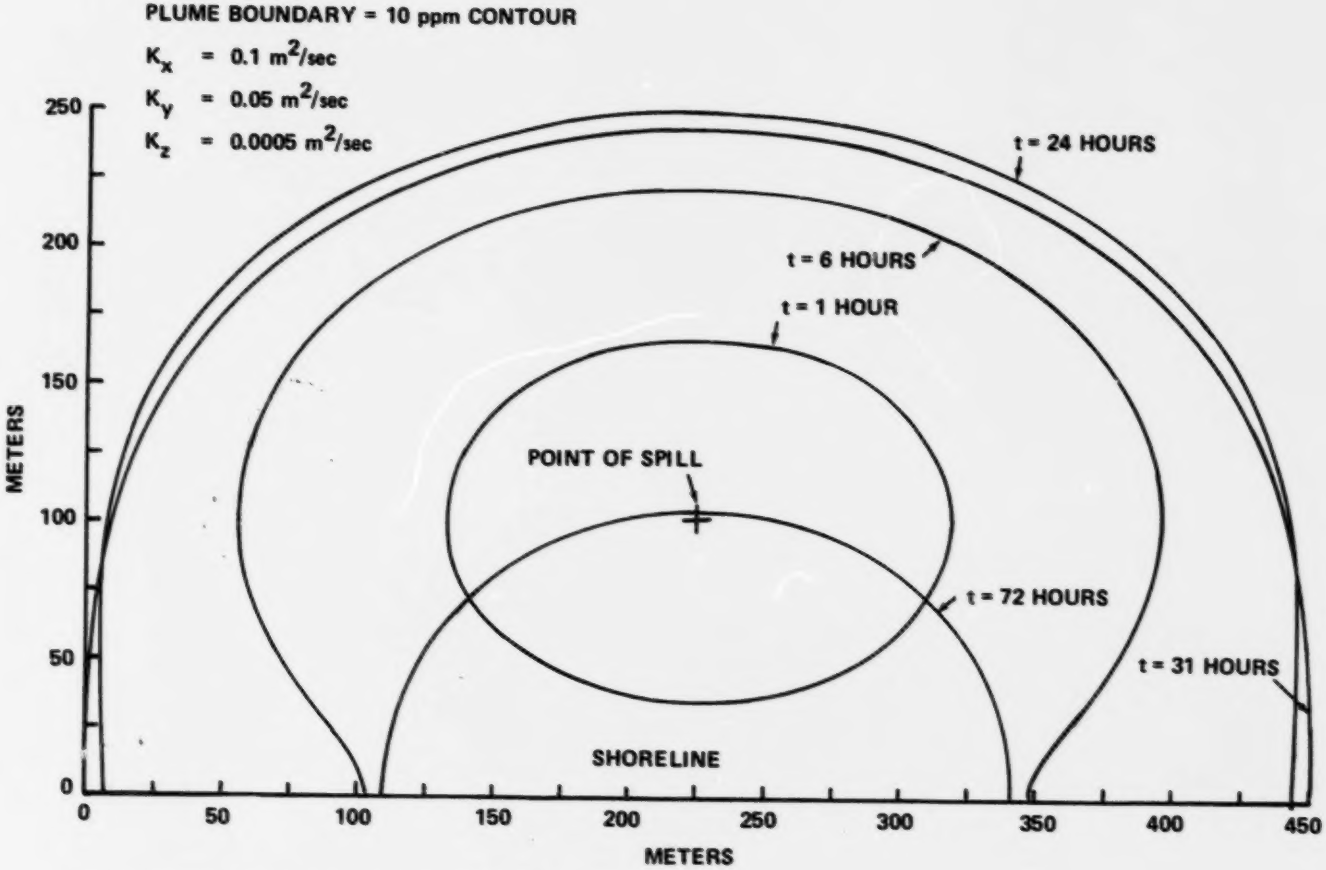


Figure 30 DISPERSION OF A 5000 GALLON PHENOL SPILL IN A NONFLOWING WATER BODY

for extreme accuracy in predicted data, it appears that a simple model such as described above could serve adequately for the calculations. Initial calculations could be made with assumed values of dispersion coefficients that are based solely on experience of the operator. Simultaneously, field data could be gathered on, for example, concentration as a function of position and rough isopleths could be plotted. Comparison could then be made of these rough isopleths and model-predicted contours to determine the nature of the error in the assumed dispersion coefficients. Adjustments could be made until a reasonable fit is achieved and the values of the coefficients thus selected could be used to make predictions for longer times in the future. Repetition of the procedure could provide upgraded predictions and account for different circumstances as they change with time or position in the water body.

During the course of the above modeling study, a parallel analytical effort was directed toward developing a flow model which would permit the analysis of not only the concentration distribution of the pollutant in the water body but also the analysis of the mean, variance, skewness and kurtosis of the concentration distribution. In addition, the model would require very simple numerical techniques to obtain solutions.

The mathematical model generated in this parallel effort was derived from the basic diffusion equation for a passive contaminant in a moving environment. In addition to considering diffusion, the possibility of incorporating a chemical reaction effect was included. This was considered to be of importance for the present study since the effect of a treatment on the dispersing pollutant was of interest. Since the scope of this analytical effort was to be limited, a two-dimensional model was considered realistic.

Consider a two-dimensional stream, as shown in Figure 31, with a velocity profile U(z). Let it be assumed that the turbulent transport of material

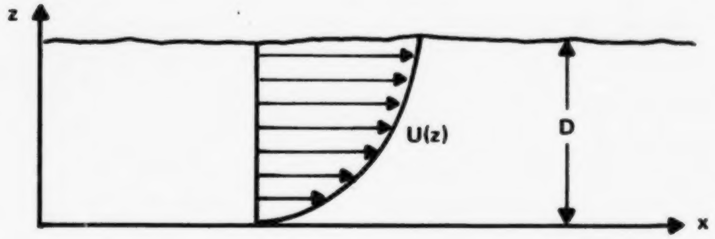


Figure 31 TWO-DIMENSIONAL STREAM

parallel to the axis can be described by eddy diffusivity coefficients K_x and K_z. Let K_x and K_z be independent of x and t and be at most functions of z. If the concentration field of the passive contaminant is written as C(x,z,t), the governing differential equation may be written as (Ref. 1):

$$\frac{\partial C}{\partial t} + U(z)\,\frac{\partial C}{\partial x} = \frac{\partial}{\partial x}\,(K_x\,\frac{\partial C}{\partial x} + \frac{\partial}{\partial z}\,(K_z\,\frac{\partial C}{\partial z}) + R(C) \qquad (13)$$

The term R(C) is considered the reaction term which is to be included when a treatment is added to the dispersing pollutant. Equation (13) is in dimensional form which is not convenient for analysis; therefore, let us introduce the following dimensionless variables:

$x^* = x/D$; $z^* = z/D$; $U^* = U/\overline{U}$ where $\overline{U}$ is the mean velocity across the section; $t^* = t/T$, $T = D/\overline{U}$: ${K_x}^* = K_x/K$, ${K_z}^* = K_z/K$; $K \equiv (\frac{D^2}{T}) = \frac{D^2\overline{U}}{D} = D\overline{U}$

$C^* = C/C_{REF}$; $R^* = R/R_{REF}$.

Equation (13) now takes the form

$$\frac{\partial C^*}{\partial t^*} + U^*\,\frac{\partial C^*}{\partial x^*} = \frac{\partial}{\partial x^*}\,({K_x}^*\,\frac{\partial C^*}{\partial x^*}) + \frac{\partial}{\partial z^*}\,({K_z}^*\,\frac{\partial C^*}{\partial z^*}) + R^* \qquad (14)$$

In discussions to follow, Equation (14) will be considered; however, the asterisks will be dropped. It is desired to solve Equation (14) for the case in which there is a sudden spill occurring at time t = 0, and no transport of material across the boundaries z = 0 and z = 1. Since in general U(z) is a typical shear profile, the expressions K_x and K_z are functions of z and an analytic solution is not readily available. Therefore one must resort to a finite difference solution of Equation (14) on a computer. Such an approach was not within the scope of the present program. Therefore, a simplified method of solution was adopted which would retain the essentials of the dispersion reaction system but would allow simpler evaluation methods to be used.

The technique used is called the method of moments and was presented by Saffman (Ref. 2). First consider Equation (14) without the rate term R. Define the expression for the nth moment of the concentration field C(x,z,t) by $\theta_n(z,t)$

$$\theta_n(z,t) = \int_{-\infty}^{\infty} x^n\, C(x,z,t)\, dx \qquad (15)$$

The functions θ_i can be interpreted in terms of the form of the concentration distribution.

Although it is not necessary to do so in employing the moment method, the assumption was made to let K_x and K_z be constants for the cases to be considered in this program. Therefore combining Equations (14) and (15), it can readily be shown that the resulting series of equations are formed:

$$\theta_o: \quad \frac{\partial \theta_o}{\partial t} - K_z \frac{\partial^2 \theta_o}{\partial z^2} = 0$$

$$\theta_1: \quad \frac{\partial \theta_1}{\partial t} - K_z \frac{\partial^2 \theta_1}{\partial z^2} = U\,(z)\,\theta_o$$

$$\theta_2: \quad \frac{\partial \theta_2}{\partial t} - K_z \frac{\partial^2 \theta_1}{\partial z^2} = 2K_x\,\theta_o + 2\,U\,(z)\,\theta_1 \tag{16}$$

$$\theta_3: \quad \frac{\partial \theta_3}{\partial t} - K_z \frac{\partial^2 \theta_3}{\partial z^2} = 6K_x\,\theta_1 + 3\,U\,(z)\,\theta_2$$

$$\theta_4: \quad \frac{\partial \theta_4}{\partial t} - K_z \frac{\partial^2 \theta_4}{\partial z^2} = 12K_x\,\theta_2 + 4\,U\,(z)\,\theta_3$$

or in general $\dfrac{\partial \theta_n}{\partial t} - k_z \dfrac{\partial^2 \theta_n}{\partial z^2} = F_n\,(z,t)$

The equations in (16) are solved sequentially since for the nth equation F_n (z,t) involves only elements $\theta_0, \ldots, \theta_{n-1}$. The above equations are solved subject to the boundary conditions that

$\dfrac{\partial \theta_i}{\partial z} = 0$ at z = 0, 1; i.e., at the bottom of the shear

and at the free surface. It is also assumed that the contaminant is deposited in the stream instantaneously at t = 0 at x = z = 0. C_{Ref} used to nondimensionalize C(x,z,t) in Equation (13) is chosen so that

$$\int_o^1 \theta_o\,(z,t)\,dz = 1$$

The left-hand side of (16) has the form

$$L\,\theta_i = \frac{\partial \theta_i}{\partial t} - K_z \frac{\partial^2 \theta_i}{\partial z^2} \qquad i = o,1,\ldots \tag{17}$$

If one obtains the Greens function for this operator L, then the moments θ_i can be expressed by

$$\theta_i = \int_o^t \int_o^1 G(z,z', t-T)\, F_i\, (z_1' T)\, dz' d\,T \tag{18}$$

where $G(z,z', t-T)$ is the Greens function. Thus it can be seen that the original problem of solving Equation (14) has been reduced to a problem of quadrature rather than finite differences and should in theory be simple to perform. The function $G(z,z', t-T)$ has been developed for an analogous heat transfer problem in Reference 3 and is therefore readily available. The first four moments θ_0, θ_1, θ_2, θ_3 have been programmed on a computer.

Before passing on to a discussion of the calculated moments of the concentration distribution subject to dispersion alone, let us consider a possible means of incorporating a sink or consumption rate term. Since the method of moments is inherently limited to a linear problem, the form of rate term must be linear. Therefore for the present work this rate was taken to be proportional to the concentration itself. That is

$$R = k\ C(x,z,t) \tag{19}$$

where $R_{REF} = C_{REF}$, since laboratory measurements of k were available for certain reactions. Physically, this reaction can be interpreted as follows: at some time T after the initial spill has occurred, the treatment is dispersed uniformly over the zone in which the pollutant is found.

The concentration at each point decreases (as a result of treatment) at a rate proportional to the concentration. The inclusion of (19) into Equation (14) and the subsequent development of the moment equations proceeds in a straightforward manner. Equations similar to (16) result except the operator defined in (17) is replaced with the operator

$$L' = \left\{ \frac{\partial}{\partial t} - K_z \frac{\partial^2}{\partial z^2} + k \right\} \tag{20}$$

such that

$$L'\,\theta_i = F_i \tag{21}$$

where the right-hand side F_i has the same form as the right-hand side of (16). If a transformation $\theta_i = e^{-kt}\bar{\theta}_i$ is defined, the system (21) may be reduced to the set:

$$\frac{\partial \bar{\theta}_i}{\partial t} - K_z \frac{\partial^2 \theta_i}{\partial z^2} = F_i\ (z,t) \tag{22}$$

which has the identical form as the set (16). Thus one may proceed as follows when analyzing a dispersing reacting system where R is given by (19): (i) Compute the solution θ_i to (16) subject to the boundary conditions for the nonreacting system for $0 \leqslant t \leqslant T$; i.e., if a treatment is added at a time the solution takes the form τ

$$0 \leqslant t \leqslant \tau \qquad \theta_i\ (z,t)$$

$$\tau < t \leqslant T \qquad \bar{\theta}_i\ (z,t) = \theta_i\ (z,t)\, e^{-k(t-\ )}$$

where θ_i is given by the output of the computer program. This scheme permits the analysis of a number of treatment situations to be applied for effect on a single computer run. Noting that the variation of dimensionalizing parameters also permits consideration of a number of physical cases for a single value of a dimensionless constant, it is clear that the present formulation can yield a tremendous amount of physical insight for a single computer run.

In order to be able to translate the meaning of the variables θ_o, $\theta_1, \ldots,$ θ_3 into a physical interpretation on the quantity of interest, the concentration distribution, the following parameters were introduced.

Mean $m = \theta_1/\theta_o.$

Variance $\sigma = \left[\left(\frac{\theta_2}{\theta_o}\right) - \left(\frac{\theta_1}{\theta_o}\right)^2\right]^{1/2}$

Skewness $\gamma_1 = \frac{\left[\left(\frac{\theta_3}{\theta_o}\right) - 3\left(\frac{\theta_1}{\theta_o}\right)\left(\frac{\theta_2}{\theta_o}\right) + 2\left(\frac{\theta_1}{\theta_o}\right)^3\right]}{\left[\left(\frac{\theta_2}{\theta_o}\right) - \left(\frac{\theta_1}{\theta_o}\right)^2\right]^{3/2}}$

Kurtosis $$\gamma 2 = \left[\left\{ \frac{\left[\frac{\theta_4}{\theta_o} - 4\left(\frac{\theta_1}{\theta_o}\right)\left(\frac{\theta_3}{\theta_o}\right) + 6 \left(\frac{\theta_1}{\theta_o}\right)^2 \left(\frac{\theta_2}{\theta_o}\right) - 3 \left(\frac{\theta_1}{\theta_o}\right)^4 \right]}{\left[\theta_2/\theta_o - \left(\frac{\theta_1}{\theta_o}\right)^2 \right]^2} \right\} - 3 \right]$$

The values of the parameters m, σ, γ_1 and γ_2 characterize the general features of (C(x,z,t). For example, the mean, m, can be viewed as describing the movement of the centroid of the concentration distribution at a particular value of z. The variance, σ, provides a measure of how the pollutant in each layer is dispersing relative to its centroid.

The skewness and kurtosis of a distribution relate the symmetry of the distribution about the centroid and the behavior of the concentration distribution far from the centroid, respectively.

An example of the mean and the variance behavior for two sets of physical parameters are shown in Figures 32 and 33, respectively. The physical parameters for the cases considered are

Case 1.		Case 2.	
K_x	$= 5.15$	K_x	$= 5.15$
K_{γ}	$= 5.1 \times 10^{-3}$	K_z	$= 5.15 \times 10^{-4}$
$U(z)$	$= z^{1/7}$	$U(z)$	$= z^{1/7}$
z	$= 0.408$	z	$= 0.408$

Recall in interpreting these cases the dimensionless variables K_x, K_z, U(z) and z have the definitions:

$$K_x = \frac{\tilde{K}_x}{D\bar{U}}, \quad K_z = \frac{\tilde{K}_z}{D\bar{U}}, \quad U(z) = \tilde{U}(z)/\bar{U}, \quad z = \tilde{z}/D$$

where quantities with $\sim$ are dimensional. As a result, the above two cases can be considered appropriate for a number of physically realistic situations with different values of the parameters $\tilde{K}_x$, $\tilde{K}_z$, $\tilde{U}(z)$, D, and $\bar{U}$. The only restriction is that the combinations must yield values of the parameters used in Case 1 or 2.

Detailed discussion of the mean, variance, skewness, kurtosis, examples of the effect of treatment for realistic values of k (in Equation (19)), as well as a comparison of the dilution effect versus the neutralization effect on the concentration, will be included in the detailed report on modeling.

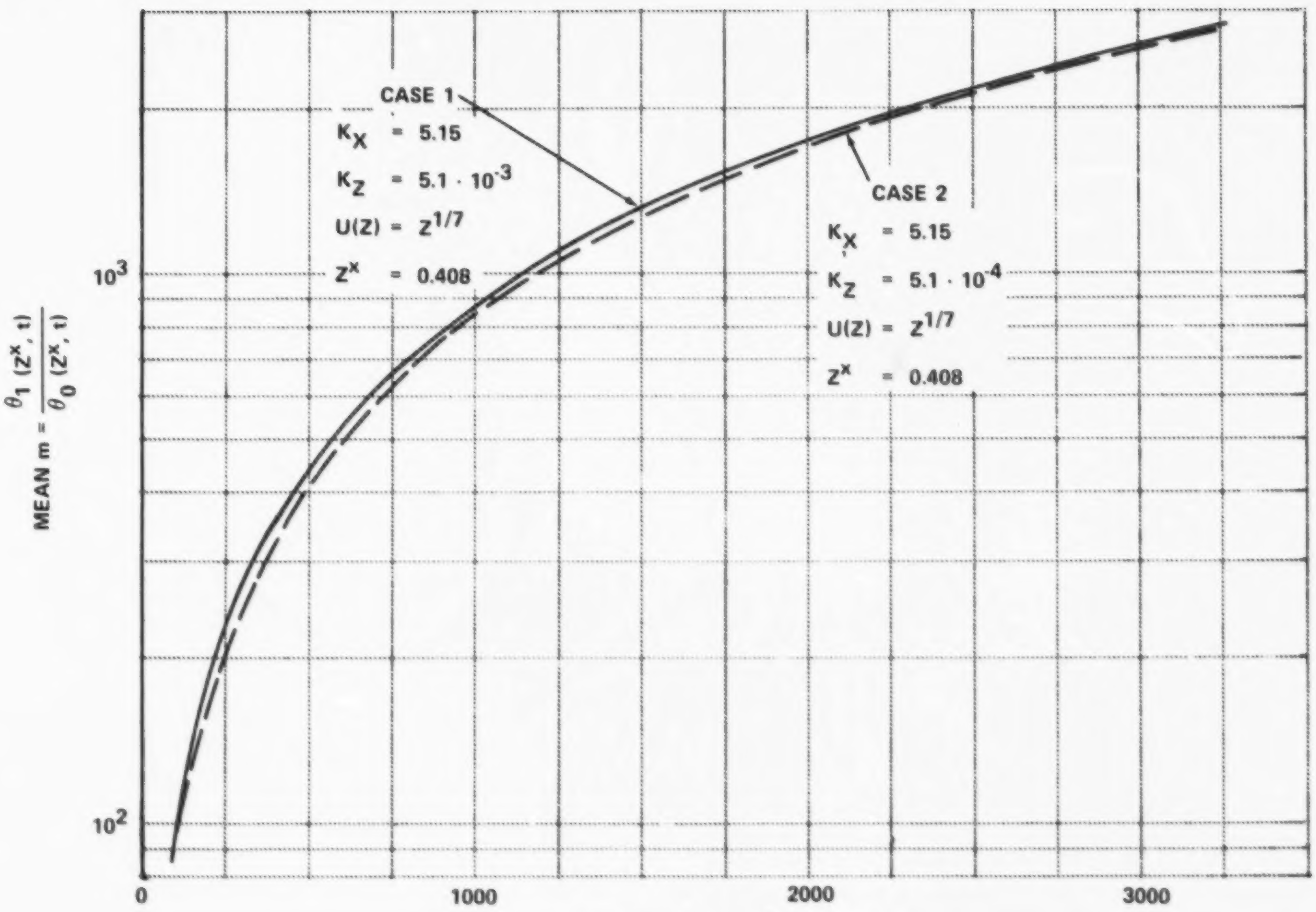


Figure 32 MEAN, $m = \frac{\theta_1}{\theta_0} (Z^x, t)$ vs t

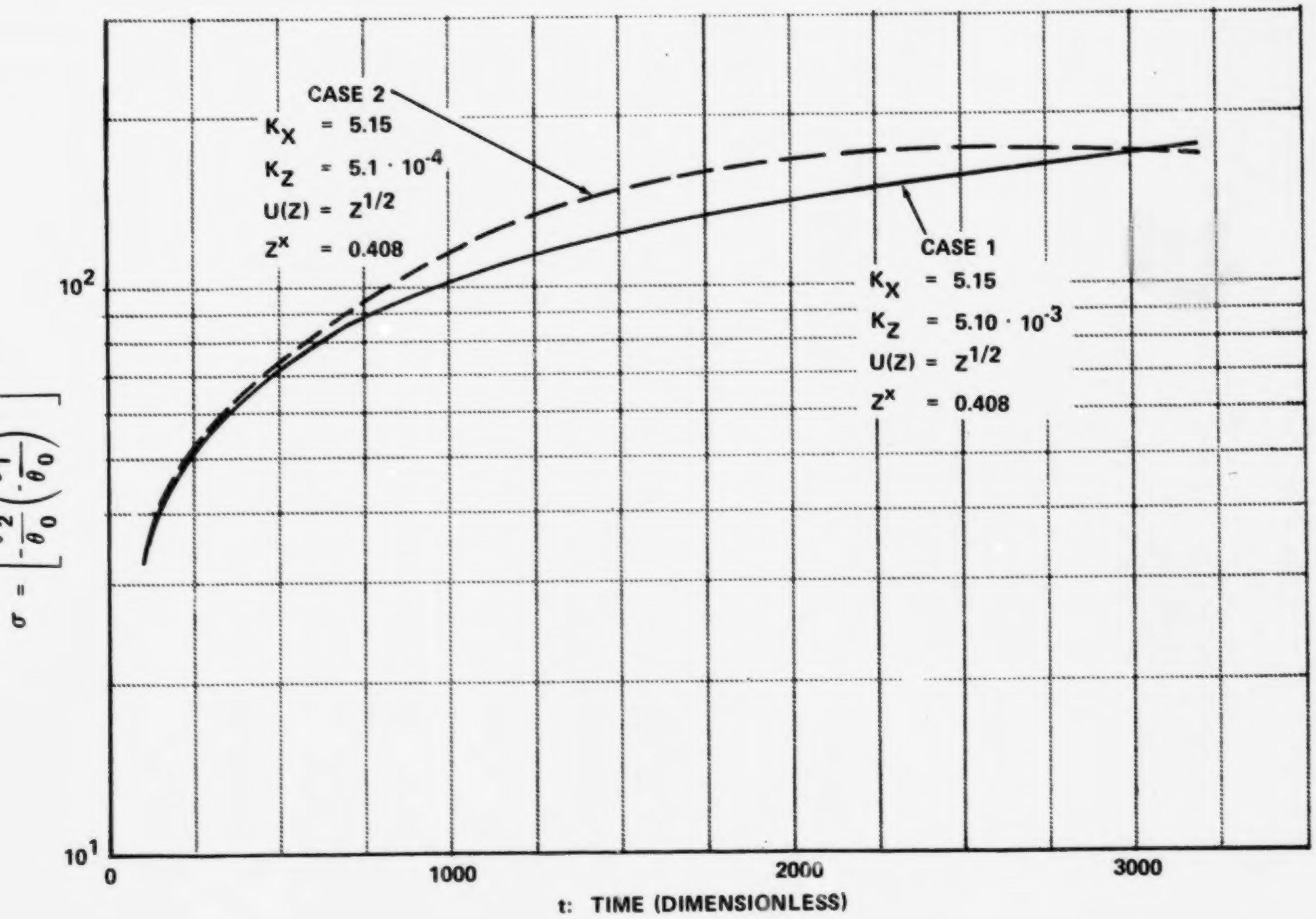


Figure 33 VARIANCE σ vs TIME

SECTION 13

HAZARDOUS CHEMICALS/COUNTERMEASURES

The matrix presented in this section is a compilation of recommended procedures for treating and controlling some 250 recognized hazardous liquids having a high probability of being involved in spills into or near watercourses. The chemicals are listed in alphabetical order. After each compound name is an "instant recognition" symbol designed to trigger in the minds of an environmental control team the selection of specific countermeasures to combat spills of that compound, that selection depending for the most part on the physical behavior of the compound in water (e.g., floats vs sinks and soluble vs insoluble) as well as its chemical nature.

The symbols shown are in the form of arrows whose thickness and orientation visually suggest the recommended treatment. A bold upright arrow, for example, identifies those liquids which are lighter than water and essentially water insoluble. The hazardous spill control team should therefore immediately consider the application of oil booming and skimming as the most effective technology to control such a spill in a watercourse. Conversely, a dense arrow pointing downward indicates that the material is heavier than water and essentially water insoluble (ten parts per million or less solubility) in which case lagooning, trenching, and sump or vacuum pumping should be considered to localize and remove that spilled substance.

A less dense arrow curving upward (i.e., toward the surface) indicates to the investigator that liquids so marked in the matrix are lighter than water and soluble in the water. He will thus recognize immediately that massive spills of such a substance will be mostly localized at, or immediately below, the water surface, and that the greatest plume dimension (as the spill spreads) will remain near the surface. Oil booming and skimming technology will be effective in early stages of such spills. Carbon adsorption, neutralization or precipitation would be required for the portion of the spill that is in solution. The most difficult-to-treat, hazardous chemical is one identified by an arrow which curves first downward and then upward to indicate that the substance is heavier than water and highly water soluble (greater than 10 ppm, when known toxic levels are less than or equal to this concentration). The maximum plume dimensions of this spreading pollutant mass will occur at the stream bottom and the most useful countermeasures will be vacuum pumping of the concentrated pools in the stream bottom soon after spill occurrence followed by activated carbon adsorption, neutralization, and/or precipitation.

The first column to the right of the instant recognition symbols shows the hazard rating of each substance as taken from previously reported work by the Environmental Protection Agency. These numbers range from 1 to 250, with the lower numbers indicating the greater hazards. The ratings were deduced from a computer program and series of algorithms which took into account such factors as the abundance of each material manufactured and transported, and its relative toxicity. The subscripts "a" and "b" appended to some of the ratings in the column denote which of the essentially water-soluble liquids are lighter than water (a) and heavier than water (b).

The matrix also shows the solubility of each liquid in water at normally encountered temperatures, the density of the liquid, and (when known either from our own studies or from other sources) the approximate lower concentrations of the chemical in water that kill fish of some specie.

The remainder of the countermeasure matrix specifies the individual countermeasures which are effective for controlling that chemical if spilled on the ground or into water. The eventual goal of any spill treatment is either the complete neutralization or the removal of the spilled material to eliminate hazardous and esthetic consequences. The immediate goals of treatment will frequently be to provide for the safety of personnel and property. In many spills the major hazards will involve toxic vapors and potential fire. These hazards must be considered first. The spilled material should be identified and appropriate medical and fire fighting personnel consulted immediately. Citizens may have to be evacuated from the affected area and proper equipment made available to protect the spill treatment teams. The application of fluro-carbon-water foams will be useful to minimize the evaporation of spilled material, and thereby reduce both the toxic and fire hazard for those materials so indicated in the matrix.

Another objective of the treatment will often be to prevent the spread of the spilled material. A variety of common-sense mechanical countermeasures may be obvious to even the untrained worker. Solids that have been spilled on the ground may be covered with plastic sheets, for example, to prevent dissolution in rainwater. Trenches may be dug for the same purpose or to arrest the surface flow of spilled liquids. Such countermeasures are applicable to spills of virtually any material and frequently may be applied before the arrival of special facilities.

The use of mechanical barriers is lumped in the matrix with chemical barriers, such as antiwetting agents that minimize ground percolation and arrest surface flow. More testing is required before specific chemical barriers can be recommended, however.

Other specific treatments of land spills included in the matrix are those which eliminate hazards without removing the material (neutralization of acids and bases and precipitation of heavy metals) and those which immobilize the spill and alter its form to facilitate mechanical removal (use of gelling agents and powdered materials to absorb the liquid bulk).

Countermeasures which are effective against hazardous materials spilled into water are also shown. Countermeasures for floating liquids include the use of natural barriers or oil spill control booms to limit spill motion for that class of materials that float on water; the use of surface active agents to compress floating materials into smaller areas or move them from otherwise inaccessible areas; and the injection of the "universal gelling agent" to solidify liquids that are either free floating, compressed by surface active agents, or trapped in booms. As with land spills, the use of mechanical means to remove the immobilized masses of pollutants is required after any of these treatments. Removal should be accomplished as soon as possible to minimize aquatic damage.

For liquids which are more dense than water, the effective countermeasures include the use of natural deep water pockets, excavated lagoons, or sandbag barriers to trap the dense material at the stream bottom before removing it with suction hoses while it is still in its liquid state. Alternatively, the "universal gelling agent" can be injected to solidify the trapped mass in place for subsequent removal by standard dredging methods.

For those materials of an acidic or basic nature, the countermeasures indicated on the matrix include the neutralization with weak acids and bases, as appropriate, as the safest possible technique. Highly water-soluble materials, especially those which are more dense than water, disperse rapidly throughout the water volume. For most of these materials the countermeasures are limited to the application of activated carbon or ion exchange resins. To avoid secondary pollution problems in either case, the treatment materials must be packaged in such a way as to permit their complete removal by mechanical means.

In the case of spills of soluble heavy metals salts, which are also more dense than water, the application of stoichiometric amounts of sodium sulfide solutions is recommended to precipitate the heavy metals as their sulfide ores. Because of the potential secondary pollution, this treatment is recommended only for small spills except where special equipment is available for measuring the local pollutant concentration and metering the treatment solution applied at that location.

CODE

↑ FLOATS, WATER INSOLUBLE
↓ SINKS, WATER INSOLUBLE
↗ FLOATS, WATER SOLUBLE
⤵ SINKS, WATER SOLUBLE

MATERIAL NAME (ALPHABETICAL)		IT'S HAZARD RATING (LOW NUMBERS INDICATE HIGH HAZARD)	IT'S SOLUBILITY IN WATER IN (PARTS PER MILLION)	ITS DENSITY (GRAMS PER MILLILITER)	CONCENTRATIONS GREATER THAN THIS ARE KNOWN TO KILL FISH (PARTS PER MILLION)	IF IT SPILLS ON THE GROUND, THE COUNTERMEASURES DOTTED ● BELOW ARE EFFECTIVE						IF IT SPILLS INTO WATER, THE COUNTERMEASURES DOTTED ● BELOW ARE EFFECTIVE										MATERIAL NAME (ALPHABETICAL)
						NEUTRALIZATION WITH LIME OR SODIUM BICARBONATE	NEUTRALIZATION WITH VINEGAR OR DILUTE ACID	APPLICATION OF FLUOROCARBON WATER FOAM TO DIMINISH VAPOR AND FIRE HAZARD AND/OR PROVIDE WET DOWN	FORM MECHANICAL AND/OR CHEMICAL BARRIERS TO PREVENT SPREAD OF MATERIAL	APPLICATION OF UNIVERSAL GELLING AGENT TO IMMOBILIZE THE SPILL	APPLICATION OF FLY ASH OR CEMENT POWDER TO ABSORB THE LIQUID BULK	USE NATURAL BARRIERS OR OIL SPILL CONTROL BOOMS TO LIMIT SPILL MOTION	USE NATURAL DEEP WATER POCKETS, DUG LAGOONS OR SAND BAG BARRIERS TO TRAP MATERIAL AT BOTTOM	USE SURFACE ACTIVE AGENTS TO COMPRESS AND THICKEN SPILLED MATERIAL	REMOVE TRAPPED MATERIAL WITH SUCTION HOSES	INJECT UNIVERSAL GELLING AGENT TO SOLIDIFY TRAPPED MASS AND INCREASE EFFECTIVENESS OF BOOMS	IF SOLUBILIZED, APPLY ACTIVATED CARBON AT 10X THE SPILL AMOUNT OVER REGION OCCUPIED BY 10 ppm OR GREATER CONCENTRATIONS	IF SOLUBILIZED, APPLY SODIUM SULFIDE SOLUTION IN STOICHIOMETRIC AMOUNTS TO PRECIPITATE HEAVY METALS	NEUTRALIZE WITH LIME OR BICARBONATE	NEUTRALIZE WITH DILUTE ACID OR WITH REMOVABLE STRONG ACID	USE MECHANICAL DREDGES OR LIFTS TO REMOVE IMMOBILIZED MASSES OF POLLUTANTS AND PRECIPITATES	
ACETALDEHYDE	↗	90	50 000	0.783	50	●			●	●	●	●		●	●	●	●		●		●	ACETALDEHYDE
ACETIC ACID	⤵	83	50 000	1.05	100	●			●	●	●								●			ACETIC ACID
ACETIC ANHYDRIDE	⤵	107	500 000	1.087	100	●			●	●	●								●			ACETIC ANHYDRIDE
ACETONE	↗	100	50 000	0.792	10 000			●	●	●	●				●	●					●	ACETONE
ACETONE CYANOHYDRIN	↗	11	1 000	0.932	1			●	●	●	●	●		●	●	●	●		●		●	ACETONE CYANOHYDRIN
ACETONITRILE	↗	80	50 000	0.78	1 000			●	●	●	●	●		●	●	●	●				●	ACETONITRILE
ACETOPHENONE	⤵	130	5 560	1.03				●	●	●	●						●				●	ACETOPHENONE
ACIDS, ACYLHALIDES & ANHYDRIDES	⤵	57	50 000	1.1		●		●	●	●	●						●		●		●	ACIDS, ACYLHALIDES & ANHYDRIDES
2,4-D ACID	↗	33	100	0.8	200	●			●	●	●	●		●	●	●	●		●		●	2,4-D ACID
2,4-D ACID ESTERS - SALTS	↗	30	25 000	0.9		●			●	●	●	●		●	●	●	●		●		●	2,4-D ACID ESTERS - SALTS
2,4,5 T ACID	⤵	143	100	1.1		●			●	●	●						●		●		●	2,4,5 T ACID
2,4,5 T ACID ESTERS - SALTS	⤵	138	1 000	1.1		●			●	●	●						●		●		●	2,4,5 T ACID ESTERS - SALTS
ACRYLIC ACID	⤵	129	50 000	1.06	1	●			●	●	●					●	●		●		●	ACRYLIC ACID
ACRYLONITRILE	↗	4	5 000	0.8	10				●	●	●	●		●	●	●	●				●	ACRYLONITRILE
ADIPIC ACID	⤵	200	10 000	1.1	200	●			●	●	●						●		●		●	ADIPIC ACID
ALCOHOLS MONOHYDRIC (UNSUBST)	↗	62	100	0.8					●	●	●	●		●	●	●	●				●	ALCOHOLS, MONOHYDRIC (UNSUBST)
ALCOHOLS MONOHYDRIC ESTERS	↗		10 000	0.8					●	●	●	●		●	●	●	●				●	ALCOHOLS, MONOHYDRIC-ESTERS
ALCOHOLS ESTERS POLYHYDRIC	⤵	168	50 000	1.2				●	●	●	●					●	●				●	ALCOHOLS, ESTERS, POLYHYDRIC
ALDEHYDES AND KETONES	↗	64	50 000	0.8		●		●	●	●	●	●		●	●	●	●				●	ALDEHYDES AND KETONES
ALDRIN TOXAPHENE GROUP	↑	18	0.01	0.8	0.05				●	●	●	●		●	●						●	ALDRIN TOXAPHENE GROUP
ALUMINUM FLUORIDE	⤵	72	50 000	3.07					●									●			●	ALUMINUM FLUORIDE
ALUMINUM SULFATE (ALUM)	⤵	20	310 000	2.71	200				●									●			●	ALUMINUM SULFATE (ALUM)
AMINES, TOTAL	↗	10	50 000	0.7			●		●	●	●	●		●	●	●	●			●	●	AMINES, TOTAL
AMMONIA	↗	1	50 000	0.807	5		●		●								●			●	●	AMMONIA
AMMONIA COMPOUNDS	↗	73	50 000	0.807	5		●		●	●	●						●			●	●	AMMONIA COMPOUNDS
AMMONIUM SULFATE	⤵	25	710 000	1.77	60				●								●				●	AMMONIUM SULFATE
AMMONIUM ACETATE	⤵	101	337 000	1.17	300				●								●				●	AMMONIUM ACETATE
AMMONIUM CHLORIDE	⤵	91	280 000	1.53	200				●								●				●	AMMONIUM CHLORIDE
AMMONIUM NITRATE	⤵	16	50 000	2.0	800				●								●				●	AMMONIUM NITRATE
AMMONIUM PERCHLORATE	⤵	70	50 000	1.95					●								●				●	AMMONIUM PERCHLORATE
AMYL ALCOHOL	↗	184	27 000	0.81	350			●	●	●	●	●		●	●	●	●				●	AMYL ALCOHOL
ANILINE	⤵	71	34 000	1.022	200		●	●	●	●	●						●			●	●	ANILINE
ANTIMONY COMPOUNDS	⤵	162	<0 000	3.0	10				●									●			●	ANTIMONY COMPOUNDS
ARSENIC COMPOUNDS	↓	98	1	5.73	1				●				●		●	●		●			●	ARSENIC COMPOUNDS
BARIUM CARBONATE	⤵	96	20	4.43	10 000				●									●			●	BARIUM CARBONATE
BENZALDEHYDE	⤵	42	1 000	1.06	30	●		●	●	●	●						●				●	BENZALDEHYDE

CODE
↑ FLOATS, WATER INSOLUBLE
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MATERIAL NAME (ALPHABETICAL)	CODE	IT'S HAZARD RATING (LOW NUMBERS INDICATE HIGH HAZARD)	IT'S SOLUBILITY IN WATER IN (PARTS PER MILLION)	ITS DENSITY (GRAMS PER MILLILITER)	CONCENTRATIONS GREATER THAN THIS ARE KNOWN TO KILL FISH (PARTS PER MILLION)	IF IT SPILLS ON THE GROUND THE COUNTERMEASURES DOTTED (●) BELOW ARE EFFECTIVE: NEUTRALIZATION WITH LIME OR SODIUM BICARBONATE	NEUTRALIZATION WITH VINEGAR OR DILUTE ACID	APPLICATION OF FLUOROCARBON WATER FOAM TO DIMINISH VAPOR AND FIRE HAZARD AND/OR PROVIDE HIT DOWN	FORM MECHANICAL AND/OR CHEMICAL BARRIERS TO PREVENT SPREAD OF MATERIAL	APPLICATION OF UNIVERSAL GELLING AGENT TO IMMOBILIZE THE SPILL	APPLICATION OF FLY ASH OR CEMENT POWDER TO ABSORB THE LIQUID BULK	IF IT SPILLS INTO WATER THE COUNTERMEASURES DOTTED (●) BELOW ARE EFFECTIVE: USE NATURAL BARRIERS OR OIL SPILL CONTROL BOOMS TO LIMIT SPILL MOTION	USE NATURAL DEEP WATER POCKETS, DUG LAGOONS OR SAND BAG BARRIERS TO TRAP MATERIAL AT BOTTOM	USE SURFACE ACTIVE AGENTS TO COMPRESS AND THICKEN SPILLED MATERIAL	REMOVE TRAPPED MATERIAL WITH SUCTION HOSES	INJECT UNIVERSAL GELLING AGENT TO SOLIDIFY TRAPPED MASS AND INCREASE EFFECTIVENESS OF BOOMS	IF DISSOLVED, APPLY ACTIVATED CARBON AT 10X THE SPILL AMOUNT OVER REGION OCCUPIED BY 10 ppm OR GREATER CONCENTRATION	IF DISSOLVED, APPLY SODIUM SULFIDE SOLUTION IN STOICHIOMETRIC AMOUNTS TO PRECIPITATE HEAVY METALS	NEUTRALIZE WITH LIME OR BICARBONATE	NEUTRALIZE WITH DILUTE ACID OR WITH REMOVABLE STRONG ACID	USE MECHANICAL DREDGES OR LIFTS TO REMOVE IMMOBILIZED MASSES OF POLLUTANTS AND PRECIPITATES	MATERIAL NAME (ALPHABETICAL)
BENZENE	↗	6	[illegible]	0.877	35			●	●	●	●	●		●	●	●	●				●	BENZENE
BENZOIC ACID	⤵	31	100	1.32	200	●			●	●	●						●		●		●	BENZOIC ACID
BENZOYL PEROXIDE	⤵	176	10 000	1.3		●			●								●				●	BENZOYL PEROXIDE
BENZYL CHLORIDE	↓	56	0.01	1.1	10				●	●			●		●	●	●				●	BENZYL CHLORIDE
BERYLLIUM DUST	↓	146	0.01	2.0	100				●				●		●	●					●	BERYLLIUM DUST
BORIC ACID	⤵	184	10 500	1.43	2 000	●			●								●		●		●	BORIC ACID
BROMINE	⤵	162	41 700	2.93	20				●								●		●		●	BROMINE
BUTADIENE INHIBITED	↗		2	0.621					●							●			●			BUTADIENE INHIBITED
n-BUTYL ACETATE	⤵	167	10 000	1.1	45			●	●	●	●						●				●	n-BUTYL ACETATE
BUTYL ACRYLATE	↑	9a	0.1	0.89	100			●	●	●	●	●		●	●	●					●	BUTYL ACRYLATE
BUTYL ALCOHOL, N AND ISO	↗	44	125 000	0.8	1 000			●	●	●	●	●		●	●	●	●				●	BUTYL ALCOHOL, N AND ISO
BUTYLAMINES	↗	130	50 000	0.74	20		●	●	●	●	●	●		●	●	●	●			●	●	BUTYLAMINES
BUTYL HYDROPEROXIDE	↗	253	1 000	0.89	40	●		●	●	●	●	●		●	●	●	●		●		●	BUTYL HYDROPEROXIDE
BUTYRIC ACID	↗	216	50 000	0.96	100	●			●	●	●	●		●	●	●	●		●		●	BUTYRIC ACID
CALCIUM ARSENATE	⤵	132	4.8	3.0	2				●				●		●	●		●			●	CALCIUM ARSENATE
CALCIUM CARBIDE	⤵	86	1 000	2.22					●													CALCIUM CARBIDE
CALCIUM CHLORIDE	⤵	125	740 000	2.15	500				●													CALCIUM CHLORIDE
CALCIUM FLUORIDE	⤵	46	16	3.18					●													CALCIUM FLUORIDE
CALCIUM HYDROXIDE	⤵		1 850	2.24			●		●											●		CALCIUM HYDROXIDE
CALCIUM HYPOCHLORITE	⤵	54	1 000	2.0					●										●			CALCIUM HYPOCHLORITE
CALCIUM NITRATE	⤵	219	56 000	2.5	3 000				●													CALCIUM NITRATE
CALCIUM PHOSPHATE, DIBASIC	⤵	157	10 000	3.0					●													CALCIUM PHOSPHATE, DIBASIC
CARBON DISULFIDE	⤵	52	2 200	1.26	100			●	●		●						●		●		●	CARBON DISULFIDE
CARBON TETRACHLORIDE	⤵	76	800	1.585	100			●	●	●	●						●				●	CARBON TETRACHLORIDE
CHLORINE (LIQUIFIED)	⤵	12	50 000	3.2	0.08				●		●						●		●		●	CHLORINE (LIQUIFIED)
CHLOROBENZENE	⤵	141	400	1.1	20			●	●	●	●						●				●	CHLOROBENZENE
CHLOROFORM	⤵	121	5 000	1.5	10			●	●	●	●						●				●	CHLOROFORM
CHLOROMETHANE	↗	122	8 000	0.952				●	●	●	●					●	●				●	CHLOROMETHANE
CHLOROSULFONIC ACID	⤵	5	1 000	1.8		●		●	●	●	●						●		●		●	CHLOROSULFONIC ACID
CHROMIC ACID	⤵	63	1 000 000	2.7	50	●			●	●	●						●		●		●	CHROMIC ACID
CITRIC ACID	⤵	108	10 000	1.54	800	●			●	●	●		●				●		●		●	CITRIC ACID
COPPER SULFATE	⤵	96	1 000	3.6	0.5				●									●			●	COPPER SULFATE
CRESOLS, TOTAL	⤵	200	31 000	1.0	10	●		●	●	●	●	●	●	●	●	●	●		●		●	CRESOLS, TOTAL
CUMENE	↑	3a	0.01	0.88	1			●	●	●	●	●		●	●	●					●	CUMENE
CYCLOHEXANE	↑	1a	0.01	0.77	15 000			●	●	●	●	●		●	●	●					●	CYCLOHEXANE
CYCLOHEXANONE	↗	148	24 000	0.94	1			●	●	●	●	●		●	●	●	●				●	CYCLOHEXANONE

CYCLOHEXYL ALCOHOL	↗	186	56 700	0.94	1			●	●	●	●	●		●	●	●	●				●	CYCLOHEXYL ALCOHOL
CYCLOHEXYLAMINE	↗	99	1 000	0.81				●	●	●	●	●		●	●	●	●			●	●	CYCLOHEXYLAMINE
DDT	↑	16	0.01	0.82	0.01				●		●	●		●	●	●	●				●	DDT
DECYL ALCOHOL	↑	64	0.1	0.82	10 000			●	●	●	●	●		●	●	●	●				●	DECYL ALCOHOL
DIBROMOCHLOROPROPANE	↶	202	100	1.2	20			●	●	●	●						●				●	DIBROMOCHLOROPROPANE
DIBUTYL PHTHALATE	↶	105	400	1.0	1 000			●	●	●	●						●				●	DIBUTYL PHTHALATE
DICHLOROBENZENE	↶	123	145	1.3	5			●	●	●	●						●				●	DICHLOROBENZENE
DICHLORODIFLUOROMETHANE	↓		0.01	1.4						●			●				●				●	DICHLORODIFLUOROMETHANE
DIETHANOLAMINE	↶	165	50 000	1.09	100		●	●	●	●	●						●			●	●	DIETHANOLAMINE
DIETHYLAMINE	↗	100	215 000	0.71	1000			●	●	●	●	●		●	●	●	●			●	●	DIETHYLAMINE
DIETHYLENE GLYCOL	↶	184	50 000	1.13	32 000			●	●	●	●						●				●	DIETHYLENE GLYCOL
DINITRO ANILINE	↓	76	0.01	1.6			●	●	●	●	●		●		●	●	●			●	●	DINITRO ANILINE
DIOCTYL PHTHALATES	↓	58	10	1.2				●	●	●	●		●		●	●	●				●	DIOCTYL PHTHALATES
DIPROPYLENE GLYCOL	↶	205	50 000	1.02	1 000			●	●	●	●						●				●	DIPROPYLENE GLYCOL
DIVINYL BENZENE	↑	94	0.01	0.93				●	●	●	●	●		●	●	●					●	DIVINYL BENZENE
DNBP	↗	156	100	0.9				●	●	●	●	●		●	●	●	●				●	DNBP
DODECYL BENZENE	↗	136	10 000	0.9	10			●	●	●	●	●		●	●	●	●				●	DODECYL BENZENE
DODECYL MERCAPTAN	↗	58	1 000	0.8				●	●	●	●	●		●	●	●	●				●	DODECYL MERCAPTAN
DYES TOTAL	↶	23	50 000	1.0	5				●	●	●	●		●	●	●	●				●	DYES TOTAL
EPICHLOROHYDRIN	↓	86	0.01	1.2	1			●	●	●	●	●				●	●				●	EPICHLOROHYDRIN
ETHYL ALCOHOL (ETHANOL)	↗	90	50 000	3.70	1 000			●	●	●	●	●		●	●	●	●				●	ETHYL ALCOHOL (ETHANOL)
ETHANOLAMINES	↗	144	50 000	0.8	75		●	●	●	●	●	●		●	●	●	●				●	ETHANOLAMINES
ETHERS TOTAL	↗	37	50 000	0.9	1 000			●	●	●	●	●		●	●	●	●			●	●	ETHERS TOTAL
ETHYL ACETATE	↗	175	86 000	0.9	1 000			●	●	●	●	●		●	●	●	●				●	ETHYL ACETATE
ETHYL ACRYLATE	↗	76	100	0.92	100	●		●	●	●	●	●		●	●	●	●				●	ETHYL ACRYLATE
ETHYLAMINES	↗	114	50 000	0.7	30			●	●	●	●	●		●	●	●	●			●	●	ETHYLAMINES
ETHYL BENZENE	↗	86	140	0.86	50			●	●	●	●	●		●	●	●	●				●	ETHYL BENZENE
ETHYL CHLORIDE	↗	175	5 740	0.92				●	●	●	●	●		●	●	●	●				●	ETHYL CHLORIDE
ETHYL ESTERS ALL GRADES	↗	187	50 000	0.8				●	●	●	●	●		●	●	●	●				●	ETHYL ESTERS ALL GRADES
ETHYL FORMATE	↗	295	50 000	0.92		●		●	●	●	●	●		●	●	●	●		●		●	ETHYL FORMATE
ETHYLENE	↗	132	300	0.001	20				●								●				●	ETHYLENE
ETHYLENEDIAMINE	↗	92	50 000	0.96	30		●	●	●	●	●	●		●	●	●	●			●	●	ETHYLENEDIAMINE
ETHYLENE DICHLORIDE	↓	16	0.01	1.1	150			●	●	●	●		●		●	●	●				●	ETHYLENE DICHLORIDE
ETHYLENE GLYCOL	↶	177	50 000	1.1	10 000				●	●	●						●				●	ETHYLENE GLYCOL
ETHYLENE OXIDE	↗	160	50 000	0.882	150				●								●				●	ETHYLENE OXIDE
ETHYLENIMINE	↗	178	50 000	0.83	1		●	●	●	●	●	●		●	●	●	●			●	●	ETHYLENIMINE
ETHYLHEXYL ACRYLATE	↗	211	10 000	0.89	140	●		●	●	●	●	●		●	●	●	●				●	ETHYLHEXYL ACRYLATE
FATTY ACIDS	↑	40	10	0.9	5			●	●	●	●	●		●	●	●					●	FATTY ACIDS
FERBAM (FERMATE) PESTICIDE	↗	156	100	0.9	1				●		●	●		●	●	●	●				●	FERBAM (FERMATE) PESTICIDE
FERROUS SULFATE	↶	38	1 000	3.1	500				●									●			●	FERROUS SULFATE
FLUORINE HYDROFLUORIC ACID	↗	66	50 000	0.081	40	●			●		●	●							●			FLUORINE HYDROFLUORIC ACID
FORMALDEHYDE	↗	22	50 000	0.016	10	●		●	●	●	●	●		●	●	●	●		●		●	FORMALDEHYDE
FORMIC ACID	↗	215	50 000	0.815	260	●			●	●	●						●		●		●	FORMIC ACID
FUMARIC ACID	↶	201	7 000	1.64	500	●			●	●	●						●		●		●	FUMARIC ACID
FUNGICIDES ACYCLIC	↗	115	100	0.9					●	●	●	●		●	●	●	●				●	FUNGICIDES ACYCLIC
FUNGICIDES MISCELLANEOUS	↗	110	100	0.8	0.060				●	●	●	●		●		●	●				●	FUNGICIDES MISCELLANEOUS
FUNGICIDES TOTAL CYCLIC	↑	26	0.01	0.9	0.009				●	●	●	●		●	●	●					●	FUNGICIDES TOTAL CYCLIC

CODE

↑ FLOATS WATER INSOLUBLE
↓ SINKS WATER INSOLUBLE
↗ FLOATS WATER SOLUBLE
⤵ SINKS WATER SOLUBLE

MATERIAL NAME (ALPHABETICAL)	CODE	IT'S HAZARD RATING (LOW NUMBERS INDICATE HIGH HAZARD)	IT'S SOLUBILITY IN WATER IN (PARTS PER MILLION)	ITS DENSITY (GRAMS PER MILLILITER)	CONCENTRATIONS GREATER THAN THIS ARE KNOWN TO KILL FISH (PARTS PER MILLION)	IF IT SPILLS ON THE GROUND THE COUNTERMEASURES DOTTED ● BELOW ARE EFFECTIVE						IF IT SPILLS INTO WATER THE COUNTERMEASURES DOTTED ● BELOW ARE EFFECTIVE										MATERIAL NAME (ALPHABETICAL)
						NEUTRALIZATION WITH LIME OR SODIUM BICARBONATE	NEUTRALIZATION WITH VINEGAR OR DILUTE ACID	APPLICATION OF FLUOROCARBON WATER FOAM TO DIMINISH VAPOR AND FIRE HAZARD AND/OR PROVIDE WET DOWN	FORM MECHANICAL AND/OR CHEMICAL BARRIERS TO PREVENT SPREAD OF MATERIAL	APPLICATION OF UNIVERSAL GELLING AGENT TO IMMOBILIZE THE SPILL	APPLICATION OF FLY ASH OR CEMENT POWDER TO ABSORB THE LIQUID BULK	USE NATURAL BARRIERS OR OIL SPILL CONTROL BOOMS TO LIMIT SPILL MOTION	USE NATURAL DEEP WATER POCKETS DUG LAGOONS OR SAND BAG BARRIERS TO TRAP MATERIAL AT BOTTOM	USE SURFACE ACTIVE AGENTS TO COMPRESS AND THICKEN SPILLED MATERIAL	REMOVE TRAPPED MATERIAL WITH SUCTION HOSES	INJECT UNIVERSAL GELLING AGENT TO SOLIDIFY TRAPPED MASS AND INCREASE EFFECTIVENESS OF BOOMS	IF SOLUBILIZED APPLY ACTIVATED CARBON AT 10X THE SPILL AMOUNT OVER REGION OCCUPIED BY 10 ppm OR GREATER CONCENTRATIONS	IF SOLUBILIZED APPLY SODIUM SULFIDE SOLUTION IN STOICHIOMETRIC AMOUNTS TO PRECIPITATE HEAVY METALS	NEUTRALIZE WITH LIME OR BICARBONATE	NEUTRALIZE WITH DILUTE ACID OR WITH REMOVABLE STRONG ACID	USE MECHANICAL DREDGES OR LIFTS TO REMOVE IMMOBILIZED MASSES OF POLLUTANTS AND PRECIPITATES	
FURFURAL	⤵	75	83 100	1.16	20	●		●	●	●	●						●				●	FURFURAL
FURFURYL ALCOHOL	⤵	185	50 000	1.12	1			●	●	●	●						●				●	FURFURYL ALCOHOL
GLYCERINE	⤵	204	50 000	1.2	10 000			●	●	●	●						●				●	GLYCERINE
GLYOXAL	⤵	220	50 000	1.14	1 000			●	●	●	●						●					GLYOXAL
HEPTANE MIXED	↗	36	52	0.68	1 000			●	●	●	●	●		●	●	●	●				●	HEPTANE MIXED
HERBICIDES - PLANT HORMONES ACYCLIC	↗	148	100	0.8					●	●	●	●		●	●	●	●				●	HERBICIDES - PLANT HORMONES ACYCLIC
HERBICIDES - PLANT HORMONES CYCLIC	↗	22	100	0.9	100				●	●	●	●		●	●	●	●				●	HERBICIDES - PLANT HORMONES CYCLIC
HERBICIDES MISCELLANEOUS CYCLIC	↗	66	1 000	0.9	100				●	●	●	●		●	●	●	●				●	HERBICIDES MISCELLANEOUS CYCLIC
HEXAMETHYLENEDIAMINE	↗	47	1 000	0.8			●	●	●	●	●	●		●	●	●	●			●	●	HEXAMETHYLENEDIAMINE
HEXANE	↗	56	138	0.66	1 000			●	●	●	●	●		●	●	●	●				●	HEXANE
HEXYL ALCOHOL	↗	196	5 900	0.81	200			●	●	●	●	●		●	●	●	●				●	HEXYL ALCOHOL
HYDROCARBONS HALOGENATED	⤵	28	50 000	1.1				●	●	●	●						●				●	HYDROCARBONS HALOGENATED
HYDROCHLORIC ACID	⤵	40	50 000	1.63	100	●			●		●								●			HYDROCHLORIC ACID
HYDROGEN CYANIDE	↗	43	50 000	0.687	0.05	●			●		●	●		●	●	●	●		●		●	HYDROGEN CYANIDE
HYDROGEN PEROXIDE	⤵	158	50 000	1.46	10	●			●		●								●			HYDROGEN PEROXIDE
HYDROGEN SULFIDE	↗		50 000	0.02					●										●			HYDROGEN SULFIDE
HYPOCHLORITES	⤵	53	1 000	1.1	1	●		●	●	●	●						●		●		●	HYPOCHLORITES
INSECTICIDES MISCELLANEOUS ACYCLIC	↗	67	1 000	0.8					●	●	●	●		●	●	●					●	INSECTICIDES MISCELLANEOUS ACYCLIC
INSECTICIDES MISCELLANEOUS CYCLIC	↑	6	0.01	0.8	0.003				●	●	●	●		●	●	●					●	INSECTICIDES MISCELLANEOUS CYCLIC
INSECTICIDES - RODENTICIDES CYCLIC	↑	3	0.01	0.8	0.003				●	●	●	●		●	●	●					●	INSECTICIDES - RODENTICIDES CYCLIC
ISOBUTANE	↑		0.01	0.6					●	●	●											ISOBUTANE
ISOCYANURATES CHLORINATED	⤵	45	10 000	1.2		●			●	●	●						●		●		●	ISOCYANURATES CHLORINATED
ISOOCTYL ALCOHOL	↗	184	10 000	0.8	1			●	●	●	●	●		●	●	●	●					ISOOCTYL ALCOHOL
ISOPENTANE	↑		0.01	0.6					●	●	●											ISOPENTANE
ISOPRENE	↑	15	0.06	0.78	100				●	●	●	●		●	●	●					●	ISOPRENE
ISOPROPYL ACETATE	↗	214	30 800	0.870	1 000			●	●	●	●	●		●	●	●	●				●	ISOPROPYL ACETATE
ISOPROPYL ACETONE	↗	210	19 000	0.8				●	●	●	●	●		●	●	●	●				●	ISOPROPYL ACETONE
ISOPROPYL ALCOHOL	↗	150	50 000	0.78	900			●	●	●	●	●		●	●	●	●				●	ISOPROPYL ALCOHOL
ISOPROPYL ETHER	↗	212	2 000	0.72	100			●	●	●	●	●		●	●	●	●				●	ISOPROPYL ETHER
LACTIC ACIDS	⤵	211	10 000	1.2	500	●			●	●	●						●		●		●	LACTIC ACIDS
LAUROYL PEROXIDE	↓	136	0.1	2.0	50	●			●		●		●		●	●					●	LAUROYL PEROXIDE
LEAD ARSENATE	⤵	64	1 000	1.3	25				●									●			●	LEAD ARSENATE
LEAD COMPOUNDS	⤵	50	50 000	5.0	0.5				●									●			●	LEAD COMPOUNDS
LINDANE	↗	76	50 000	0.9	0.1				●			●		●	●	●	●				●	LINDANE
MAGNESIUM COMPOUNDS	⤵	211	1 000	2.0	400				●									●			●	MAGNESIUM COMPOUNDS
MAGNESIUM SULFATE	⤵	163	260 000	2.66	10 000				●									●			●	MAGNESIUM SULFATE
MALEIC ANHYDRIDE	⤵	145	50 000	0.93	100	●			●	●	●						●				●	MALEIC ANHYDRIDE

MERCURY	↓	196	0.0005	13.54					●				●		●	●					●	MERCURY
MERCURY COMPOUNDS	↓	79	0.01	3.0	0.02				●				●		●	●	●	●			●	MERCURY COMPOUNDS
MERCURY FUNGICIDES	↓	83	0.01	1.2					●				●		●	●	●	●			●	MERCURY FUNGICIDES
METHYL ACETATE	↗	206	1,000	0.9				●	●	●				●	●	●	●				●	METHYL ACETATE
METHYL ALCOHOL (METHANOL)	↗	2	80,000	0.79	15,000			●	●	●	●	●		●	●	●	●				●	METHYL ALCOHOL (METHANOL)
METHYLAMINE	↗	87	1,000	0.66	20		●	●	●	●	●	●		●	●	●	●			●	●	METHYLAMINE
METHYL BROMIDE	↶	116	900	1.7	1,000			●	●	●	●						●				●	METHYL BROMIDE
METHYL ETHYL KETONE	↗	112	353,000	0.805	5,000	●		●	●	●	●	●		●	●	●	●				●	METHYL ETHYL KETONE
METHYL METHACRYLATE	↗	125	1,000	0.94	100	●		●	●	●	●	●		●	●	●	●				●	METHYL METHACRYLATE
METHYL PARATHION	↗	61	50	0.9	0.1			●	●	●	●	●		●	●	●	●				●	METHYL PARATHION
MONO ETHANOLAMINE	↶	180	50,000	1.01	50		●	●	●	●	●						●			●	●	MONO ETHANOLAMINE
MORPHOLINE	↗	287	50,000	0.9998	100		●	●	●	●	●	●		●	●	●	●			●	●	MORPHOLINE
NABAM	↗	156	100	0.8					●	●	●	●		●	●	●	●			●	●	NABAM
NAPHTHALENE	↶	51	30	1.15	10			●	●	●	●						●			●	●	NAPHTHALENE
NICKEL COMPOUNDS	↶	47	642,000	3.0	1				●									●			●	NICKEL COMPOUNDS
NICKEL SULFATE	↶	131	293,000	3.68	15				●									●			●	NICKEL SULFATE
NITRIC ACID	↶	21	50,000	1.5	1	●			●		●		●						●			NITRIC ACID
NITROANILINE	↶	160	1,260	1.44	25		●	●	●	●	●						●				●	NITROANILINE
NITROBENZENE	↶	80	1,000	1.19	20			●	●	●	●						●				●	NITROBENZENE
NITROPHENOL	↶	17	16,000	1.6	10	●		●	●	●	●						●		●		●	NITROPHENOL
NITROUS OXIDE	↗	118	1,000	0.001					●										●			NITROUS OXIDE
NONENE	↑	46	1.6	0.7	1,000			●	●	●	●	●		●	●							NONENE
NONYL PHENOL	↑	13	10	0.94	1	●		●	●	●	●	●		●	●	●						NONYL PHENOL
OXALIC ACID	↶	181	50,000	1.9	2,000	●		●	●	●	●						●		●		●	OXALIC ACID
PARATHION	↗	130	25	0.9	0.1			●	●	●	●	●		●	●	●	●				●	PARATHION
PENTACHLOROPHENOL	↶	80	100	1.98	0.2			●	●	●	●	●		●	●	●	●				●	PENTACHLOROPHENOL
PENTANE	↗	166	360	0.62	100			●	●	●	●	●		●	●	●						PENTANE
PERCHLORIC ACID	↶	86	1,000	1.8	1				●	●	●								●			PERCHLORIC ACID
PERCHLOROETHYLENE	↓	26	0.01	1.6	1			●	●	●	●		●		●	●	●				●	PERCHLOROETHYLENE
PESTICIDES - INSECTICIDES ACYCLIC	↗	35	50,000	0.8	0.1				●	●	●	●		●	●	●	●				●	PESTICIDES - INSECTICIDES ACYCLIC
PHENOL	↶	1	67,000	1.07	15	●		●	●	●	●						●		●		●	PHENOL
PHENYL MERCURIC ACETATE	↑	100	0.02	0.9				●	●	●	●	●		●	●		●				●	PHENYL MERCURIC ACETATE
PHOSPHORIC ACID	↶	58	5,480,000	1.8	1	●			●		●								●			PHOSPHORIC ACID
PHOSPHORUS	↓	29	3.0	1.8	0.1				●				●		●	●						PHOSPHORUS
PHOSPHORUS OXYCHLORIDE	↗	142	50,000	0.6		●			●													PHOSPHORUS OXYCHLORIDE
PHOSPHORUS PENTASULFIDE	↶	9	203	2.02					●													PHOSPHORUS PENTASULFIDE
PHOSPHORUS TRICHLORIDE	↶	124	50,000	1.5	100				●													PHOSPHORUS TRICHLORIDE
PHTHALIC ANHYDRIDE	↶	165	10,000	1.5		●		●	●	●	●						●		●		●	PHTHALIC ANHYDRIDE
POTASSIUM COMPOUNDS	↶	111	50,000	2.0	500				●													POTASSIUM COMPOUNDS
POTASSIUM HYDROXIDE	↶	115	970,000	2.04	50				●		●									●		POTASSIUM HYDROXIDE
POTASSIUM IODIDE	↶	96	1,275,000	3.13	10				●													POTASSIUM IODIDE
POTASSIUM PYROPHOSPHATE	↶	189	50,000	2.33					●										●			POTASSIUM PYROPHOSPHATE
POTASSIUM SULFATE	↶	188	120,000	2.66	800				●													POTASSIUM SULFATE
PROPIONIC ACID	↗	182	50,000	0.992	100	●			●	●	●	●		●	●	●	●		●		●	PROPIONIC ACID
PROPYL ACETATE	↗	170	18,900	0.887	100			●	●	●	●	●		●	●	●	●				●	PROPYL ACETATE
N-PROPYL ALCOHOL (N-PROPANOL)	↗	113	50,000	0.8	200			●	●	●	●	●		●	●	●	●				●	N-PROPYL ALCOHOL (N-PROPANOL)

CUES ↑ FLOATS WATER INSOLUBLE ↓ SINKS WATER INSOLUBLE ↗ FLOATS WATER SOLUBLE ⤵ SINKS WATER SOLUBLE MATERIAL NAME (ALPHABETICAL)		IT'S HAZARD RATING (LOW NUMBERS INDICATE HIGH HAZARD)	IT'S SOLUBILITY IN WATER IN PARTS PER MILLION	ITS DENSITY (GRAMS PER MILLILITER)	CONCENTRATIONS GREATER THAN THIS ARE KNOWN TO KILL FISH (PARTS PER MILLION)	IF IT SPILLS ON THE GROUND THE COUNTERMEASURES DOTTED (●) BELOW ARE EFFECTIVE						IF IT SPILLS INTO WATER THE COUNTERMEASURES DOTTED (●) BELOW ARE EFFECTIVE										MATERIAL NAME (ALPHABETICAL)
						NEUTRALIZATION WITH LIME OR SODIUM BICARBONATE	NEUTRALIZATION WITH VINEGAR OR DILUTE ACID	APPLICATION OF FLUOROCARBON WATER FOAM TO DIMINISH VAPOR AND FIRE HAZARD AND/OR PROVIDE NET DOWN	FORM MECHANICAL AND/OR CHEMICAL BARRIERS TO PREVENT SPREAD OF MATERIAL	APPLICATION OF UNIVERSAL GELLING AGENT TO IMMOBILIZE THE SPILL	APPLICATION OF FLY ASH OR CEMENT POWDER TO ABSORB THE LIQUID BULK	USE NATURAL BARRIERS OR OIL SPILL CONTROL BOOMS TO LIMIT SPILL MOTION	USE NATURAL DEEP WATER POCKETS, BAG LAGOONS OR SAND BAG BARRIERS TO TRAP MATERIAL AT BOTTOM	USE SURFACE ACTIVE AGENTS TO COMPRESS AND THICKEN SPILLED MATERIAL	REMOVE TRAPPED MATERIAL WITH SUCTION HOSES	INJECT UNIVERSAL GELLING AGENT TO SOLIDIFY TRAPPED MASS AND INCREASE EFFECTIVENESS OF BOOMS	IF SOLUBILIZED APPLY ACTIVATED CARBON AT 10X THE SPILL AMOUNT OVER REGION OCCUPIED BY 10 PPM OR GREATER CONCENTRATIONS	IF SOLUBILIZED APPLY SODIUM SULFIDE SOLUTION IN STOICHIOMETRIC AMOUNTS TO PRECIPITATE HEAVY METALS	NEUTRALIZE WITH LIME OR BICARBONATE	NEUTRALIZE WITH DILUTE ACID OR WITH REMOVABLE STRONG ACID	USE MECHANICAL DREDGES OR LIFTS TO REMOVE IMMOBILIZED MASSES OF POLLUTANTS AND PRECIPITATES	
PROPYLAMINES	↗	106	50 000	0.7	20		●	●	●	●	●	●		●	●		●			●	●	PROPYLAMINES
PROPYLENE	↗		200	0.507					●	●	●	●				●	●					PROPYLENE
PROPYLENE DICHLORIDE	⤵	173	2 270	1.16				●	●	●	●						●				●	PROPYLENE DICHLORIDE
PROPYLENE GLYCOL	⤵	174	50 000	1.00	1 000			●	●	●	●						●				●	PROPYLENE GLYCOL
PROPYLENE OXIDE	↗	100	400 000	0.8	1 000				●	●	●	●		●	●	●	●				●	PROPYLENE OXIDE
PYRIDINE	↗	48	50 000	0.9	100		●	●	●	●	●	●		●	●	●	●			●	●	PYRIDINE
SILVER CYANIDE	↓	118	0.23	3.95					●				●		●	●		●	●		●	SILVER CYANIDE
SILVER NITRATE	⤵	57	1 220 000	4.3	0.05				●				●					●	●		●	SILVER NITRATE
SODIUM METAL	↗	137	420 000	0.97					●											●		SODIUM METAL
SODIUM ACETATE	⤵	163	50 000	2.0	5 000				●											●		SODIUM ACETATE
SODIUM BORATE	⤵	164	25 100	1.73					●											●		SODIUM BORATE
SODIUM COMPOUNDS	⤵	109	50 000	2.0					●											●		SODIUM COMPOUNDS
SODIUM CARBONATE	⤵	68	20 000	2.53	100				●											●		SODIUM CARBONATE
SODIUM CHLORATE	⤵	150	790 000	3.0	10 000				●											●		SODIUM CHLORATE
SODIUM DICHROMATE AND CHROMATE	⤵	34	873 000	3.0	50				●													SODIUM DICHROMATE AND CHROMATE
SODIUM FLUORIDE	⤵	140	42 200	2.56	5				●													SODIUM FLUORIDE
SODIUM HYDROSULFITE	⤵	88	250 000	3.0	1.0				●													SODIUM HYDROSULFITE
SODIUM HYDROXIDE	⤵	54	420 000	2.13	25		●		●		●									●		SODIUM HYDROXIDE
SODIUM METHYLATE	⤵	183	50 000	2.4					●											●		SODIUM METHYLATE
SODIUM PHOSPHATE	⤵	128	70 000	3.0	750				●											●		SODIUM PHOSPHATE
SODIUM SILICATE	⤵	172	50 000	2.0	2 500		●	●	●													SODIUM SILICATE
SODIUM SULFATE	⤵	128	47 600	2.6	5 000				●													SODIUM SULFATE
SODIUM SULFIDE	⤵	38	154 000	1.9	50				●											●		SODIUM SULFIDE
SODIUM SULFITE	⤵	148	110 000	1.46	100				●											●		SODIUM SULFITE
SORBITOL	⤵	161	50 000	1.2				●	●	●	●						●				●	SORBITOL
STYRENE	↗	10	1 000	0.9	25			●	●	●	●	●		●	●	●	●				●	STYRENE
SULFUR	↓	25	0.001	1.9	1 000				●				●		●						●	SULFUR
SULFUR DIOXIDE	⤵	77	50 000	1.4	1				●										●			SULFUR DIOXIDE
SULFURIC ACID	⤵	27	50 000	1.8	5	●			●		●		●						●			SULFURIC ACID
TETRAETHYLENE GLYCOL	⤵	216	50 000	1.01	1 000			●	●	●	●						●				●	TETRAETHYLENE GLYCOL
TETRALIN	↗	105	1 000	0.9				●	●	●	●	●		●	●	●	●				●	TETRALIN
TETRAETHYL LEAD	↓	35	0.08	1.6				●	●	●	●		●		●	●	●				●	TETRAETHYL LEAD
TOLUENE	↗	61	470	0.86	50			●	●	●	●	●		●	●	●	●				●	TOLUENE
TRICHLOROETHANE	↓	46	1.0	1.3	15			●	●	●	●		●		●	●	●				●	TRICHLOROETHANE
TRICHLOROETHYLENE	⤵	121	1 000	1.4	50			●	●	●	●						●				●	TRICHLOROETHYLENE

TRICHLOROFLUOROMETHANE	↓	[illegible]	0.01	1.4	[illegible]			●	●	●	●		●		●	●	●				●	TRICHLOROFLUOROMETHANE
2,4,5 TRICHLOROPHENOL AND SALTS	↓	[illegible]	0.01	1.1	[illegible]	●		●	●	●	●		●		●	●	●		●		●	2,4,5 TRICHLOROPHENOL AND SALTS
TRIETHANOLAMINE	↗	167	15 000	0.72	20		●	●	●	●	●	●		●	●	●	●			●	●	TRIETHANOLAMINE
TRIETHYLENE GLYCOL	↖↓	197	[illegible]	1.1	1 000			●	●	●	●						●				●	TRIETHYLENE GLYCOL
TRIMETHYLAMINE	↗	[illegible]	1 000	[illegible]	250			●	●	●	●	●		●	●	●	●			●	●	TRIMETHYLAMINE
TURPENTINE	↗	151	1 000	0.85	1			●	●	●	●	●		●	●	●	●				●	TURPENTINE
UREA	↖↓	171	[illegible]	1.3	15 000		●		●								●				●	UREA
VINYL ACETATE	↗	112	20 000	0.934	25			●	●	●	●	●		●	●	●	●				●	VINYL ACETATE
VINYL CHLORIDE	↗		1 000	0.91				●	●	●	●	●		●	●	●	●				●	VINYL CHLORIDE
VINYL ETHER	↑		1	0.76				●	●	●	●			●	●	●	●				●	VINYL ETHER
XYLENES	↑	16	10	0.86	10			●	●	●	●	●		●	●	●	●				●	XYLENES
ZINC ACETATE	↖↓	192	1 000	3.0														●			●	ZINC ACETATE
ZINC CHLORIDE	↖↓	102	4 320 000	2.91	1				●									●		●	●	ZINC CHLORIDE
ZINC COMPOUNDS	↖↓	101	4 320 000	2.91	5				●									●			●	ZINC COMPOUNDS
ZINC SULFATE	↖↓	[illegible]	[illegible]	3.54	25				●									●		●	●	ZINC SULFATE

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